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Annual Performance Report for In Situ Bioremediation Operations November 2003 to September 2004, Test Area North, Operable Unit 1-07B

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ABSTRACT

This report documents the progress of the in situ bioremediation (ISB) remedial component of the Test Area North, Operable Unit 1-07B remedial action for operations performed from November 2003 through September 2004. Activities performed during this reporting period were conducted as part of the Initial Operations Phase. Two ISB strategies were implemented during this reporting period: (1) sodium lactate injections were alternated between TSF-05 and TAN-1859 on a monthly basis from November 2003 through February 2004, and (2) an alternate electron donor (AED) optimization was initiated in March 2004 to evaluate the effectiveness of whey powder in comparison to sodium lactate. The results of data collected during this reporting period indicate that the ISB remedy continues to operate effectively. Implementation of the first ISB strategy continued to maintain reducing conditions appropriate for anaerobic reductive dechlorination of trichloroethene to ethene; however, determining distribution and utilization of electron donor following injections into TAN-1859 was difficult because of vertical transport of sodium lactate within the well during the injection. Data for the second strategy, initiation of the AED optimization, are presented in this report; however, the results will be discussed upon completion of the AED optimization in June 2005.

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ACRONYMS

AED	alternate electron donor
ARD	anaerobic reductive dechlorination
bls	below land surface
COD	chemical oxygen demand
DI	deionized
DCE	dichloroethene
DNA	deoxyribonucleic acid
EPA	U.S. Environmental Protection Agency
FD/FER	Field Demonstration/Field Evaluation Report
INL	Idaho National Laboratory
IRC	INL Research Center
ISB	in situ bioremediation
MCL	maximum contaminant level
MDL	method detection limit
MS/MSD	matrix spike/matrix spike duplicate
NA	not available
NPTF	New Pump and Treat Facility
ORP	oxidation reduction potential
PCE	tetrachloroethene
PDO	Predesign Operations
PDP	Predesign Phase
PE	performance evaluation
QA	quality assurance
QC	quality control
RAWP	Remedial Action Work Plan

RPD	relative percent difference
SAM	Sample and Analysis Management
SAP	Sampling and Analysis Plan
SPME	solid-phase microextraction
TAN	Test Area North
TBD	to be determined
TCE	trichloroethene
TPR	technical procedure
USGS	United States Geological Survey
VC	vinyl chloride
VFA	volatile fatty acid
VOC	volatile organic compound

Annual Performance Report for In Situ Bioremediation Operations November 2003 to September 2004, Test Area North, Operable Unit 1-07B

1. INTRODUCTION

The purpose of this report is to document the progress of in situ bioremediation (ISB) operations at the Test Area North (TAN) Operable Unit 1-07B remedial action. This annual report provides a description of ISB activities for the reporting period November 2003 through September 2004.

1.1 Organization of Report

This report is organized into seven sections and four appendixes. Section 1 presents an overview of the ISB remedy. Section 2 describes the activities performed. Section 3 presents the results of these activities. Section 4 discusses the results collected from November 2003 through February 2004 in the context of the project objectives. Data collected during the alternate electron donor (AED) optimization (March 2004 through September 2004) are presented in Section 3 of this report, but the results will be discussed upon completion of the AED optimization in July 2005. Sections 5 and 6 present conclusions of this year's work and recommendations for additional activities. References are included in Section 7. The four appendixes (A–D) contain supporting information, as indicated throughout the main text. A CD-ROM is attached (Appendix C), which contains ISB data collected during the reporting period.

1.2 Overview of the Operable Unit 1-07B Remedy and the In Situ Bioremediation Remedial Component

Operable Unit 1-07B consists of a trichloroethene (TCE) -contaminated groundwater plume emanating from the Technical Support Facility (TSF)-05 injection well at the Idaho National Laboratory (INL). Because of the large scale and the varying contaminant concentrations within the plume, the plume has been divided into three zones (Figure 1-1): the hot spot, medial zone, and distal zone. A multi-component remedy was designed to address these three zones, as described in the *Record of Decision Amendment for the Technical Support Facility Injection Well (TSF-05) and Surrounding Groundwater Contamination (TSF-23) and Miscellaneous No Action Sites Final Remedial Action* (DOE-ID 2001). These remedies include:

- Hot spot—ISB
- Medial zone—Pump and treat
- Distal zone—Monitored natural attenuation.

In Situ Bioremediation activities have been ongoing in the hot spot since 1998. A number of operational phases were designed to measure the effectiveness of the remedy over time. The following sections provide a summary of ISB activities conducted through the previous annual report (October 2003; Section 1.2.1), the activities for the current reporting period (November 2003 through September 2004; Section 1.2.2), and future activities (October 2004 and beyond; Section 1.2.3). Table 1-1 presents an overview of the phases used for the implementation of ISB in the hot spot.

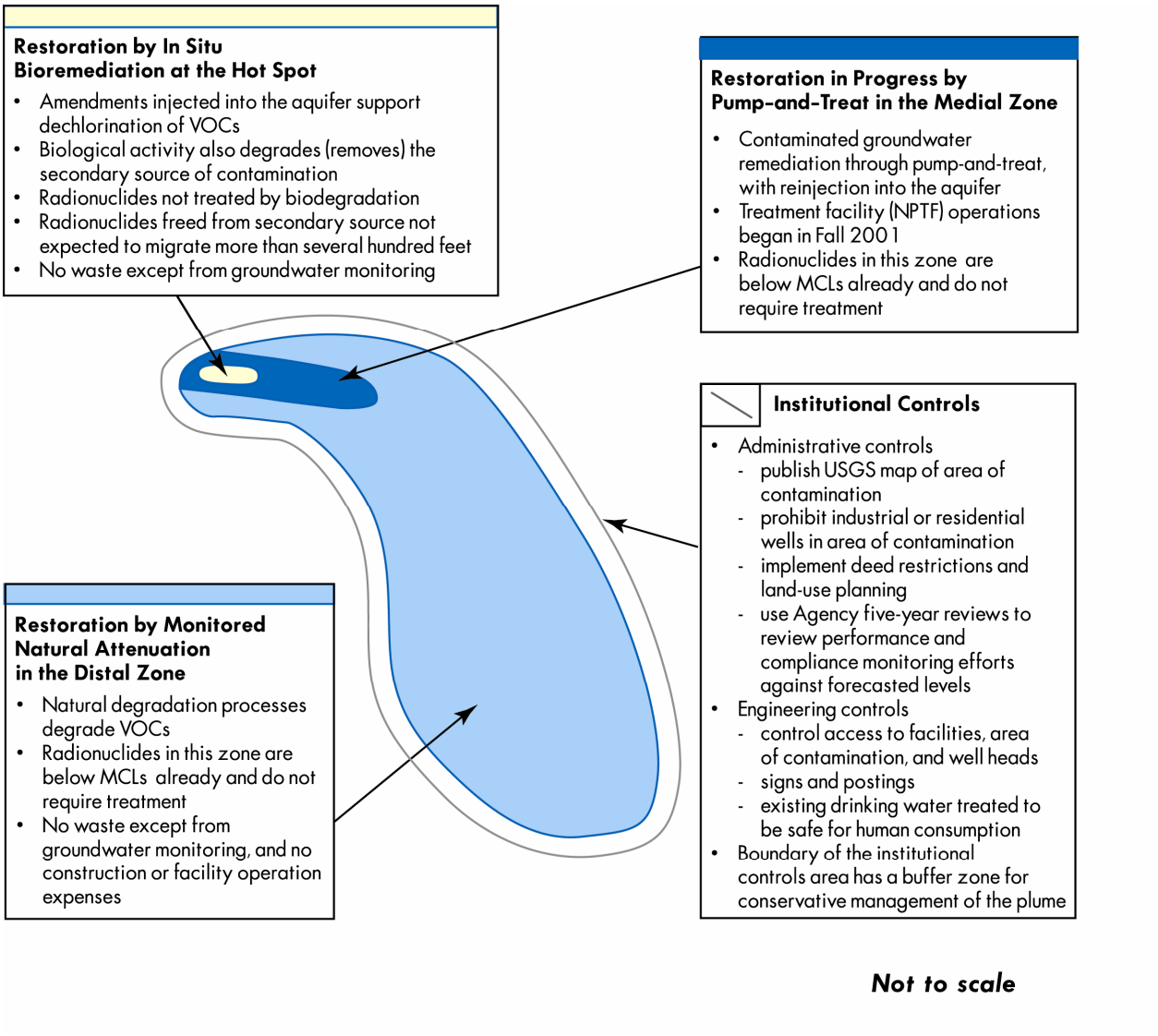

Figure 1-1. Conceptual illustration of the three zones of the trichloroethene plume.

1.2.1 Summary of In Situ Bioremediation Activities through the Previous Annual Report (October 2003)

In situ bioremediation activities began in November 1998 with the field evaluation. The overall objective of the field evaluation was to determine whether anaerobic reductive dechlorination (ARD) of TCE to the innocuous daughter product ethene could be enhanced through the addition of an electron donor (sodium lactate). Nine months of sodium lactate injections in Well TSF-05 and groundwater monitoring throughout the treatment cell produced sufficient data to conclude that ARD was significantly enhanced, and ISB was officially selected as the hot spot remedy (DOE-ID 2001). A complete discussion of the results of the field evaluation is presented in the *Field Demonstration Report, Test Area North Final Groundwater Remediation, Operable Unit 1-07B* (DOE-ID 2000).

Table 1-1. Overview of the phases used for in situ bioremediation implementation in the hot spot.

	Phase						
	Field Evaluation	Predesign Phase I	Predesign Phase II	Predesign Operations	Interim Operations	Initial Operations	Optimization and Long-Term Operations
Dates	November 1998 – September 1999	October 1999 – January 2000	February 2000 – April 2001	May 2001 – October 2002	November 2002 – October 2003	November 2003 – ongoing	TBD
Overall Objective	Determine whether TCE dechlorination could be enhanced though the addition of an electron donor.	Monitor ARD reactions under propionate fermentation conditions in the absence of regular lactate injections.	Recreate the conditions for efficient ARD observed during PDP-I.	Continue to operate ISB system while performing construction and setup of ISB injection system.		Continue system operation, while reducing downgradient flux of VOCs from the hot spot.	Continue system operation, while reducing and eventually eliminating downgradient and crossgradient flux of VOCs from the hot spot.
Operations	Small, frequent (weekly/biweekly) lactate injections; groundwater monitoring.	No lactate injections; groundwater monitoring.	Relatively large volume, infrequent (bimonthly) lactate injections; groundwater monitoring; lab studies.	Relatively large volume, infrequent (bimonthly) lactate injections; groundwater monitoring; lab studies.		Alternating monthly lactate injections in two wells for 4 months; alternate electron donor field optimization started in March 2004; groundwater monitoring.	Implement injection strategy to achieve maximum cost effectiveness; continue groundwater monitoring.
Results	Complete ARD to ethene observed; ISB selected as hot spot remedy.	ARD efficiency increased under propionate utilization conditions in the absence of lactate fermentation.	In general, good conditions for ARD maintained. However, distribution of lactate downgradient was problematic.	In general, good conditions for ARD maintained. However, complete distribution of lactate downgradient was not achieved.		TBD	TBD
Controlling Document	Field Evaluation Work Plan (DOE-ID 1998)	Field Evaluation Work Plan (DOE-ID 1998)	Field Evaluation Work Plan (DOE-ID 1998)	Predesign Operations Work Plan (DOE-ID 2002b)	RAWP (DOE-ID 2002a)	RAWP (DOE-ID-2002a)	RAWP (DOE-ID-2002a)

Table 1-1. (continued).

	Phase						
	Field Evaluation	Predesign Phase I	Predesign Phase II	Predesign Operations	Interim Operations	Initial Operations	Optimization and Long-Term Operations
Reports	FDR (DOE-ID 2000)/FER (INEEL 2000)	2001 Annual Report (INEEL 2002a)	2001 Annual Report (INEEL 2002a)	2002 Annual Report (INEEL 2003a)	2003 Annual Report (Armstrong et al. 2004)	2004 Annual Report	Annual Performance/ Compliance Reports

ARD = anaerobic reductive dechlorination

FDR/FER = Field Demonstration/Field Evaluation Report

ISB = in situ bioremediation

RAWP = Remedial Action Work Plan

TBD = to be determined

TCE = trichloroethene

VOC = volatile organic compound

Following this initial testing phase, activities shifted toward optimization of the ISB remedy. This shift began in October 1999 with Predesign Phase (PDP) -I activities, which consisted of no sodium lactate injections and continued groundwater monitoring throughout the hot spot. The objective of PDP-I was to observe how the system would respond to the absence of regular sodium lactate injections with the only available substrates being the secondary fermentation products (mainly propionate and acetate), which had accumulated to relatively high concentrations during the frequent field evaluation injections. The results indicated an increase in the efficiency of ARD reactions, as evidenced by dramatic increases in total ethene concentrations during this time. The PDP-I ended after the depletion of secondary fermentation substrates when additional lactate injections were needed to maintain nutritional requirements.

Based on the PDP-I results, an injection strategy that maximized the time of propionate utilization and minimized the time for lactate fermentation was designed for PDP-II. It was the objective of PDP-II to recreate the favorable conditions for efficient ARD observed during PDP-I and to determine the best injection strategy for later phases. PDP-II, beginning in February 2000, consisted of the injection of relatively large volumes of electron donor relatively infrequently (every 8 weeks) compared to the smaller volume, more frequent injections (weekly/bi-monthly) that were used during the field evaluation. The results of PDP-II indicated that in general, favorable conditions for ARD were created with this injection strategy; however, the distribution of electron donor to the downgradient area of the source remained problematic. A complete discussion of the results of PDP-I and PDP-II is presented in the *Operable Unit 1-07B In Situ Bioremediation Annual Performance Report for October 1999 to July 2001* (INEEL 2002a). Shortly after the onset of PDP-II, laboratory studies were initiated to evaluate alternative, potentially less expensive electron donors for their ability to support efficient ARD and to enhance degradation of the secondary source, with the objective of designing the most cost-effective remedy.

The implementation of the next phase of activities, Predesign Operations (PDO), was initiated in May 2001 with the completion of the *In Situ Bioremediation Predesign Operations Work Plan Test Area North, Operable Unit 1-07B* (INEEL 2002b). In general, the objectives of PDO were to continue the optimization of the ISB remedy through continued operations (i.e., sodium lactate injection and groundwater monitoring) and testing of various injection strategies. The results of PDO through July 2001 were presented in the Fiscal Year 2001 ISB Annual Report (INEEL 2002a). Predesign Operations activities continued through Fiscal Year 2002 with continued injection of electron donor to achieve the desired distribution and create the conditions for efficient ARD throughout the source area. The evaluation of alternate electron donors (AEDs) in laboratory studies continued from the previous reporting period. Details of PDO activities were presented in the *Annual Performance Report for In Situ Bioremediation Operations August 2001 to October 2002, Test Area North Operable Unit 1-07B* (INEEL 2003a).

The PDO phase ended in October 2002 and was followed by the Interim Operations Phase, which extended from November 2002 through October 2003. This phase was essentially a continuation of the PDO objectives and included activities designed to support a better understanding of AEDs, development of injection strategies to support the Initial Operations Phase, ISB model refinement, continued ISB sodium lactate addition, and construction of the ISB facility. The results and details of activities conducted during the Interim Operations Phase are reported in the *Annual Performance Report for In Situ Bioremediation Operations November 2002 to October 2003, Test Area North Operable Unit 1-07B* (Armstrong et al. 2004).

1.2.2 Activities for the Current Reporting Period (November 2003 through September 2004)

The completion of the ISB prefinal inspection (Building TAN-1614) for the remedial action on October 16–17, 2003 (ICP 2004) marked the start of the Initial Operations Phase. All activities performed during this reporting period (November 2003 through September 2004) were conducted as part of the Initial Operations Phase. Two ISB strategies were implemented during this reporting period based on recommendations from the Interim Operations Phase (Armstrong et al. 2004). First, sodium lactate injections were alternated between TSF-05 and TAN-1859 on a monthly basis from November 2003 through February 2004. Second, initiation of an AED optimization to evaluate the effectiveness of whey powder as an AED began in March 2004. Data collected during the AED optimization (March 2004 through September 2004) will be presented and discussed upon completion of the AED optimization in July 2005.

The *In Situ Bioremediation Remedial Action Work Plan for Test Area North Final Groundwater Remediation, Operable Unit 1-07B* (DOE-ID 2002a) and supporting documents, specifically the *In Situ Bioremediation Remedial Action Groundwater Monitoring Plan for Test Area North, Operable Unit 1-07B* (INEEL 2003b) and the *In Situ Bioremediation Operations and Maintenance Plan for Test Area North, Operable Unit 1-07B* (DOE-ID 2002b), are the governing documents for the Initial Operations Phase. Governing documents, and any changes to these documents, will be stated in each annual report. The objective of the Initial Operations Phase is to focus on reducing the flux of volatile organic compounds (VOCs) from the hot spot in the downgradient direction, as measured at TAN-28 and TAN-30A. Additionally, data will be gathered and analyzed relating to achievement of long-term performance objectives.

1.2.3 Future Activities (October 2004 and Beyond)

The Initial Operations Phase will be complete when it is determined that downgradient flux from the hot spot has been reduced such that VOC concentrations remain less than maximum contaminant levels (MCLs) at TAN-28 and TAN-30A for a period of 1 year. Following completion of the Initial Operations Phase, two additional phases will follow:

- Optimization Operations Phase—This phase will focus on reducing the flux of VOCs from the hot spot in the crossgradient direction, as measured at TAN-1860 and TAN-1861, while maintaining VOC flux reduction in the downgradient direction. During this phase, data will continue to be gathered and analyzed with regards to achievement of long-term performance objectives.

- Long-Term Operations Phase—This phase will focus on achievement of hot spot source degradation, while maintaining the reduction of VOC flux from the hot spot in the crossgradient and downgradient directions.

The ISB Remedial Action Work Plan (DOE-ID 2002a) presents a complete description and the criteria for completion of each phase, as well as performance monitoring and compliance monitoring requirements. Progress of ISB activities against these requirements will be the focus of future reports.

1.3 Reporting Period Requirements

The current reporting period is part of the Initial Operations Phase. As specified in the ISB Remedial Action Work Plan (DOE-ID 2002a), the requirements during the Initial Operations Phase are to achieve the following:

- Focus on reducing the flux of VOCs from the hot spot in the downgradient direction

- Routinely monitor performance of the ISB system with respect to indicator parameters, including VOCs, tritium, ethene/ethane/methane, redox parameters, electron donor, bioactivity, and nutrients, and determine whether operational changes are required.

As discussed in subsequent sections of this document, each of the above requirements was performed during this reporting period and implementation of the remedy will continue as part of the Initial Operations Phase.

2. ACTIVITIES PERFORMED

Activities performed during this reporting period (November 2003 through September 2004) were conducted as part of the Initial Operations Phase of the ISB remedy. Groundwater monitoring information, including the ISB monitoring well network and details of sample analyses, is described in Section 2.1. Two ISB strategies were implemented during this reporting period: (1) routine operations of alternating monthly sodium lactate injections (Section 2.2) between wells TSF-05 and TAN-1859 from November 2003 through February 2004, and (2) initiation of the AED optimization (Section 2.3) in March 2004. Other activities performed during this reporting period include multi-parameter water quality instrument monitoring (Section 2.4), water level monitoring (Section 2.5), and waste management (Section 2.6).

2.1 Groundwater Monitoring

The ISB Remedial Action Work Plan (DOE-ID 2002a) and the Groundwater Monitoring Plan (INEEL 2003b) prescribe the requirements for the extensive ISB groundwater monitoring program. This section provides a description of the monitoring well network and sample analyses for the entire reporting period. Specific details for each of the two ISB strategies are reported in Sections 2.2 (Routine Sodium Lactate Injections) and 2.3 (AED Optimization).

2.1.1 Monitoring Well Network

A total of 17 monitoring locations were routinely sampled during this reporting period. The ISB monitoring well network consists of 14 monitoring wells (Figure 2-1). Wells TSF-05 and TAN-37 utilized sampling points located at multiple depths and each sampling depth is designated with a letter (e.g., A, B, or C). Table 2-1 details the 17 monitoring locations, the depth of each sampling point, and the horizontal distance of each point from the TSF-05 injection well.

2.1.2 Sample Analyses

In general, all monitoring locations were sampled for a suite of analytes selected to provide sufficient data to evaluate ISB progress. Sampling was conducted on a monthly basis, with additional sampling events conducted during the AED optimization. During this reporting period, sample analyses were performed in the on-Site Field Laboratory, at the INL Research Center (IRC), and at off-Site laboratories.

The on-Site Field Laboratory is located in building TAN-1614 (Figure 2-1). The field laboratory is the center for all on-Site analyses and sample collection activities. Performing sample analyses on-Site allows for near real-time data for evaluating the performance of the ISB remedy. Sample analyses conducted in the field laboratory include performance level data for pH, alkalinity, ferrous iron, sulfate, phosphate, ammonia as nitrogen, and chemical oxygen demand (COD). These analyses were performed using Hach® field test kit methods for colorimeters and digital titrators. In addition, the field laboratory was used for sample preparation, handling, recordkeeping, and coordinating sample transportation to the IRC or sample shipment to off-Site laboratories.

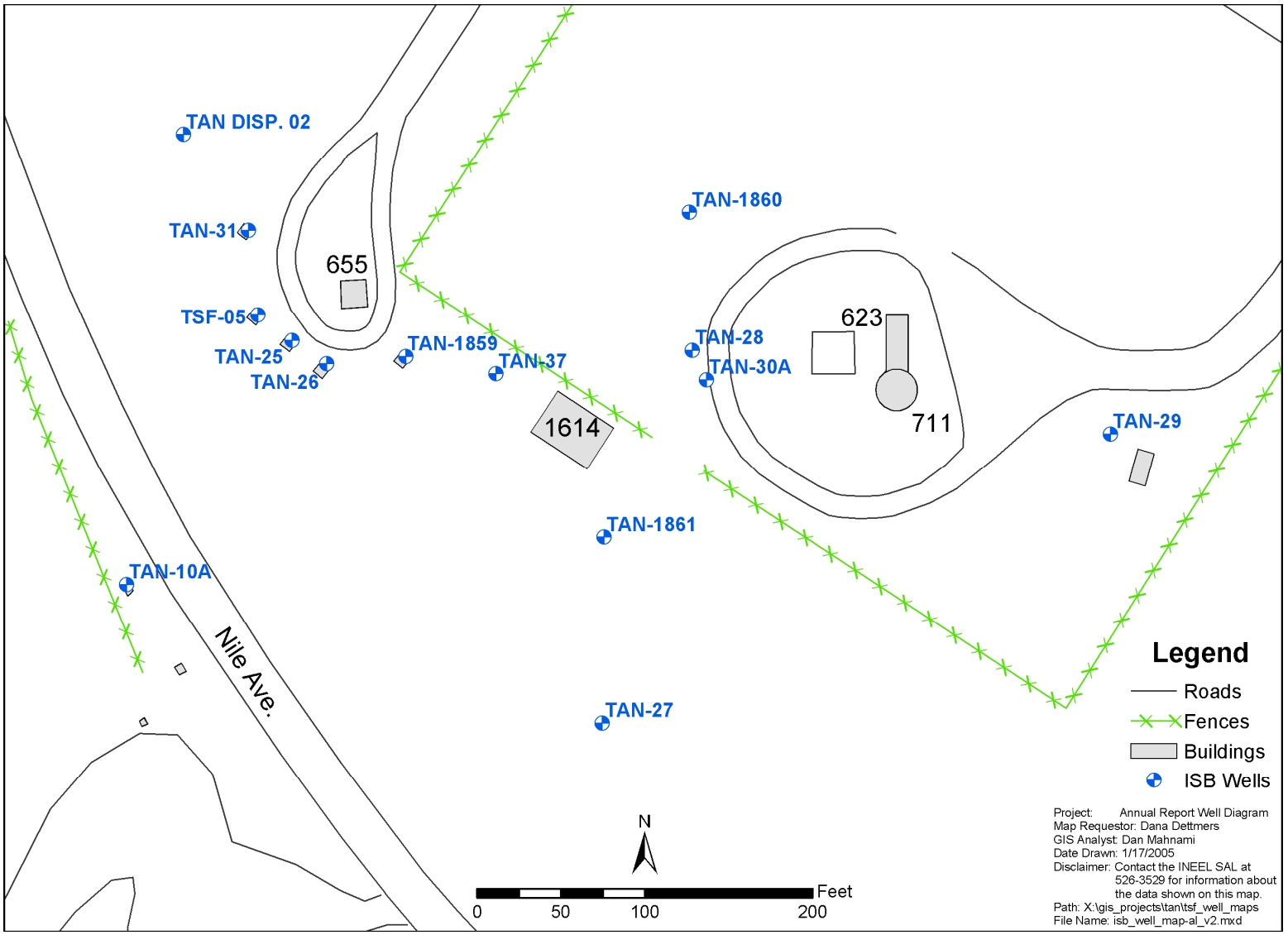

Figure 2-1. In situ bioremediation monitoring well network.

Table 2-1. Wells sampled during in situ bioremediation sampling events.

Well	Depth Sampled (ft)	Distance from TSF-05 (ft)
TSF-05A[a]	235	0
TSF-05B[a]	270	0
TAN-25	218	25
TAN-26	389	50
TAN-27	235	320
TAN-28	240	262
TAN-29	253	513
TAN-30A	313	271
TAN-31	258	50
TAN-37A[a]	240	140
TAN-37B[a]	270	140
TAN-37C[a]	375	140
TAN-10A	233	179
TAN-D2	241	115
TAN-1859	250[b]	92
TAN-1860	269	263
TAN-1861	239	246

a. Wells TSF-05 and TAN-37 are sampled at more than one depth. The letter following the well number is used to represent the sample depth.

b. Well TAN-1859 was sampled at 220 ft during the November 2003 sampling event and at 220 and 250 ft during the December 2003 sampling event. All subsequent samples from TAN-1859 were collected at 250 ft.

Samples were delivered to the IRC for analysis of VOCs using solid-phase microextraction (SPME), ethene/ethane/methane using gas chromatography/flame ionization detector, electron donor constituents using ion chromatography and gas chromatography/flame ionization detector, and microbiological samples. Off-Site sample analyses included semi-annual VOC split samples and radiological samples. Off-site VOC samples were analyzed using SW-846 Method 8260B, "Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry" (EPA 1996). Radiological samples were analyzed at commercial laboratories for tritium, strontium 90, gamma spectroscopy, and gross alpha. The off-Site commercial analytical laboratories used during this reporting period are listed in Table 2-2. Samples to be sent off-Site were gamma-screened at the INL Radiation Measurements Laboratory to ensure radiological requirements for transportation and laboratory receipt were met.

Table 2-2. Off-Site analytical laboratories used during this reporting period.

Laboratory	Analyses
Lionville Laboratory Inc., Lionville, PA	VOC splits
General Engineering Laboratories, Inc., Charleston, SC	Tritium Strontium 90 Gamma spectroscopy Gross alpha

VOC = volatile organic compound

2.2 Routine Sodium Lactate Injections (November 2003 through February 2004)

Sodium lactate injections were alternated monthly between injection wells TSF-05 and TAN-1859 from November 2003 through February 2004. This ISB strategy was based on the recommendation stated in the ISB Annual Performance Report for November 2002 through October 2003 (Armstrong et al. 2004) to test injection strategies utilizing the available injection wells. The following sections discuss injection operations (Section 2.2.1) and the monitoring schedule (Section 2.2.2).

2.2.1 Sodium Lactate Injection Operations

Sodium lactate injection operations were performed in accordance with the ISB Operations and Maintenance Plan (DOE-ID 2002b). Aqueous injections entail opening the potable water valve until the desired flowrate is observed on the flowmeter, attaching a hose and an injection pump to the amendment container, then starting the pump and adjusting the variable frequency drive to obtain the desired nominal injection rate. After the desired quantity of aqueous electron donor is injected, potable water continues to be injected for approximately 1 hour in order to rinse the injection system. The sodium lactate vendor used during this reporting period was JRW Technologies. All of the stock products were brought on-Site as 60% solution by weight (w/w) in 55-gal drums or 275-gal bulk containers.

Sodium lactate injection dates, volumes, and concentrations during the reporting period are shown in Table 2-3. The “Injection Type” column refers to the approximate volume of sodium lactate plus potable water that was injected, as well as the intended nominal sodium lactate concentration. The actual concentrations, calculated based on actual volumes injected, are presented in the “Resultant Sodium Lactate Concentration” column. Injections of approximately 12,000 gal of 6% amendment concentration (1X 6%) were performed for the first three injections of the reporting period. In order to increase sodium lactate distribution, approximately 24,000 gal of 3% amendment concentration (2X 3%) were injected on February 9, 2004.

2.2.2 Groundwater Monitoring Schedule

From November 2003 through February 2004, sampling events were conducted on a monthly basis. The descriptive data such as dates of sampling events, analyte sets, and locations sampled are identified in Tables 2-4 and 2-5 (Table 2-5 provides a key for analyte sets shown in Table 2-4). Sampling and Analysis Plan (SAP) tables (Appendix A) were used to document specific details of each sampling event. The only deviation from the SAP table was not collecting field blanks on November 11, 2003.

Table 2-3. Routine sodium lactate injections into Wells TSF-05 and TAN-1859.

Injection Date	Volume 60% (w/w) Sodium Lactate Injected (gal)	Injection Type	Total Volume Sodium Lactate Solution Injected (gal)	Resultant Sodium Lactate Concentration (%)	Combined Injection Flow Rate (gpm)	Potable Water Flush Volume (gal)
November 3, 2003 (TSF-05)	1,320	1X 6%[a]	11,916	6.0	40.2	2,160
December 1, 2003 (TAN-1859)	1,320	1X 6%	11,607	6.1	40.7	2,190
January 6, 2004 (TSF-05)	1,320	1X 6%	11,088	6.4	40.3	2,190
February 9, 2004 (TAN-1859)	1,330	2X 3%[b]	22,626	3.3	40.1	2,280

a. 1X 6% = an injection volume of approximately 12,000 gal and a 6% concentration of sodium lactate.

b. 2X 3% = an injection volume of approximately 24,000 gal and a 3% concentration of sodium lactate.

Table 2-4. In situ bioremediation groundwater monitoring events from November 2003 through February 2004.

Sampling Event	Analyte Set[a]	Sampling Location[b]
November 10–12, 2003	M, Sp	All ISB Wells
	N	All ISB Wells
	^{90}Sr, GS	TAN-1859, TAN-1860, TAN-1861 (for characterization purposes only, samples were collected from TAN-1859 at 220 ft)
	GA	TAN-1859, TAN-1860, TAN-1861 (for characterization purposes only, samples were collected from TAN-1859 at 220 ft)
December 8–10, 2003	M	All ISB Wells (samples were collected from TAN-1859 at 220 and 250 ft)
	MB	TAN-25 and TAN-37B
January 12–14, 2004	M	All ISB Wells (samples were collected from TAN-1859 at 250 ft)
	MB	TAN-25, TAN-37A, and TAN-37B
February 16–18, 2004	M	All ISB Wells (samples were collected from TAN-1859 at 250 ft)

a. The analyte set key is provided in Table 2-5.

b. All ISB wells include: TSF-05A, TSF-05B, TAN-25, TAN-26, TAN-27, TAN-28, TAN-29, TAN-30A, TAN-31, TAN-37A, TAN-37B, TAN-37C, TAN-10A, TAN-D2, TAN-1859, TAN-1860, and TAN-1861.

Table 2-5. Key for analyte sets shown in Table 2-4.

Analyte Set Code	Analytes	Analysis Location
M	**ISB monthly monitoring analyte list:** VOCs trichloroethene (TCE), tetrachloroethene (PCE), cis-1,2-dichloroethene (cis-DCE), trans-1,2-dichloroethene (trans-DCE), and vinyl chloride (VC) E/E/M P/B/A/L	IRC
	Tritium	Off-Site laboratory
	Alkalinity, ferrous iron, sulfate, COD	ISB Field Laboratory
	Gamma screens (only wells TSF-05A, TSF-05B, TAN- 25, TAN-26, TAN-31, TAN-1859 and TAN-1861)	Radiation Measurements Laboratory
N	**Nutrients:** Phosphate, ammonia	ISB Field Laboratory
MB	Microbiological research	IRC
Sp	**Splits:** VOCs E/E/M	Off-Site laboratories
^{90}Sr	Strontium-90	Off-Site laboratories
GS	Gamma spectroscopy	
GA	Gross alpha	

COD = chemical oxygen demand
E/E/M = ethene/ethane/methane
IRC = INL Research Center
ISB = in situ bioremediation
P/B/A/L = propionate/butyrate/acetate/lactate
VOC = volatile organic compound

Sample analyses details are stated in Section 2.1.2. Microbiological research samples collected from TAN-25 and TAN-37B in December 2003 and TAN-25, TAN-37A, and TAN-37B in January 2004 were used in laboratory studies performed at the IRC to assess dechlorination potential of several AEDs.

2.3 Alternate Electron Donor Optimization (March 2004 through September 2004)

The objective of the AED optimization is to evaluate if the use of whey powder for long-term ISB operations will improve system performance and decrease cost. The AED optimization was initiated in March 2004 and continues beyond the duration of this reporting period. This report includes activities performed during the first 7 months of the AED optimization, March 2004 through September 2004. The approach and requirements for performing the AED optimization are detailed in the *Alternate Electron Donor Optimization Plan for ISB Operations at Test Area North Operable Unit 1-07B* (Harris and Hall 2005).

This ISB strategy was based on the recommendation, stated in the ISB Annual Performance Report for November 2002 through October 2003 (Armstrong et al. 2004), to conduct an AED optimization involving small-scale injections into TSF-05. The results of laboratory evaluation of potential AEDs were the basis for this recommendation. The laboratory results suggested that whey powder may be a more cost-effective electron donor at TAN than sodium lactate and that an optimization should be conducted to assess the performance of whey powder in the field (Harris and Hall 2005). As previously stated in Section 1, data collected for the AED optimization (March 2004 through September 2004) are presented in this report and will be discussed upon completion of the AED optimization in July 2005. The following sections discuss electron donor injection operations (Section 2.3.1), the groundwater monitoring schedule (Section 2.3.2), and microbial characterization (Section 2.3.3).

2.3.1 Electron Donor Injection Operations

The AED optimization approach includes two baseline sodium lactate injections followed by whey powder injections. During this reporting period, the two baseline sodium lactate injections and one whey powder injection were completed. Results from baseline groundwater monitoring following sodium lactate injections are being compared to results from groundwater monitoring following whey powder injections to evaluate the performance of the two electron donors. The approach for future whey powder injections during the AED optimization is detailed in the AED Optimization Plan (Harris and Hall 2005) and may be modified if groundwater monitoring results indicate that distribution, concentration, or utilization data will not be comparable to that observed during sodium lactate injections.

Baseline sodium lactate injections were conducted (as described in Section 2.2.1) and injection dates, volumes, and concentrations are shown in Table 2-6. The initial whey powder injection (Table 2-7) was performed in accordance with the ISB Operations and Maintenance Plan (DOE-ID 2002b). Whey powder was injected at approximately 10% by weight for approximately 6 hours. The injection rate was approximately 34 gallons per minute (gpm) of both whey powder solution and potable water. The injection was followed by a potable water flush, which injected approximately 1,900 gal of potable water over a 1-hour period.

Table 2-6. Baseline sodium lactate injections for the alternate electron donor optimization.

Injection Date	Volume 60% (w/w) Sodium Lactate Injected (gal)	Injection Type	Total Volume Sodium Lactate Solution Injected (gal)	Resultant Sodium Lactate Concentration (%)	Combined Injection Flow Rate (gpm)	Potable Water Flush Volume (gal)
March 15, 2004 (TSF-05)	1,355	1X 6%[a]	12,950	5.7	41.0	2,250
May 10, 2004 (TSF-05)	1,355	1X 6%	14,162	5.2	40.0	2,202

a. 1X 6% = an injection volume of approximately 12,000 gal and a 6% concentration of sodium lactate.

Table 2-7. Whey powder injection for the alternate electron donor optimization.

Injection Date	Mass of Whey Powder Injected (lb)	Injection Type	Total Volume of Whey Powder Solution Injected (gal)	Resultant Whey Concentration (%w/w)	Combined Injection Flow Rate (gpm)	Potable Water Flush Volume (gal)
August 16, 2004 (TSF-05)	9,800	1X 10%	13,157	9.72	34	1,842

2.3.2 Groundwater Monitoring Schedule

The dates of sampling events, locations sampled, and analyte sets for groundwater monitoring events conducted from March 2004 through September 2004 are identified in Tables 2-8 and 2-9. The sampling frequency for routine ISB operations is monthly, which is conducted 1 and 5 weeks following sodium lactate injections. For the AED optimization, an increased frequency sampling schedule was implemented in order to more accurately quantify enhanced TCE dissolution from the residual source. For scheduling purposes, the day of the electron donor injection is labeled as Day 1 with sampling conducted on Days 2, 4, 8–11 (corresponds with monthly ISB sampling), 22 or 23, 36–38 (corresponds with monthly ISB sampling) and 71–73 (corresponds with monthly ISB sampling).

The SAP tables (Appendix A) provide documentation regarding specific details of each sampling event. The only deviation from the SAP tables was the gamma screen sample planned to be collected at TAN-1861 on March 23, 2004, which was not collected because the radiological designation for this well was removed. Sample analyses details are stated in Section 2.1.2. Microbial parameter samples were collected from TAN-25 for performing microbial characterization, and these results will be discussed upon completion of the AED optimization. A sample was collected to support INL research, not related to the scope of this report, from TAN-25 on July 20, 2004.

Table 2-8. Alternate electron donor ISB sampling and analysis events for the reporting period.

Date(s)	Activity (Day)	Location	Analyte Set[a]
March 15, 2004	Sodium lactate injection 1X 6% (Day 1)	TSF-05	NA
March 16, 2004	Baseline groundwater monitoring (Day 2)	TSF-05A, TSF-05B, TAN-31	AED Analysis Set
		TAN-25	AED Analysis Set, MB
March 18, 2004	Baseline groundwater monitoring (Day 4)	TSF-05A, TSF-05B, TAN-31	AED Analysis Set
		TAN-25	AED Analysis Set, MB
March 22–24, 2004	ISB sampling, monthly (Days 8–10)	TAN-27, TAN-28, TAN-29, TAN-30A, TAN-37A, TAN-37B, TAN-37C, TAN-10A, TAN-D2, TAN-1860, and TAN-1861	AED Analysis Set, ^{3}H
		TAN-1859	AED Analysis Set, ^{3}H, and GS
		TSF-05A, TSF-05B, TAN-31, and TAN-26	AED Analysis Set, ^{3}H, ^{90}Sr, and GS
		TAN-25	AED Analysis Set, ^{3}H, ^{90}Sr, GS and MB
		TAN-25	AED Analysis Set, MB
April 5, 2004	Baseline groundwater monitoring (Day 22)	TSF-05A, TSF-05B, TAN-31	AED Analysis Set
April 19–20, 2004	ISB sampling, monthly (Days 36–37)	TAN-27, TAN-28, TAN-29, TAN-30A, TAN-37A, TAN-37B, TAN-37C, TAN-10A, TAN-D2, TAN-1860, and TAN-1861	AED Analysis Set, ^{3}H
		TAN-1859	AED Analysis Set, ^{3}H, and GS
		TSF-05A, TSF-05B, TAN-31, and TAN-26	AED Analysis Set, ^{3}H, ^{90}Sr, and GS
		TAN-25	AED Analysis Set, ^{3}H, ^{90}Sr, GS and MB

Table 2-8. (continued).

Date(s)	Activity (Day)	Location	Analyte Set[a]
May 10, 2004	Sodium lactate injection 1X 6% (Day 1)	TSF-05	NA
May 11, 2004	Baseline groundwater monitoring (Day 2)	TSF-05A, TSF-05B, TAN-31	AED Analysis Set
		TAN-25	AED Analysis Set, MB
May 13, 2004	Baseline groundwater monitoring (Day 4)	TSF-05A, TSF-05B, TAN-31	AED Analysis Set
		TAN-25	AED Analysis Set, MB
May 17–19, 2004	ISB sampling, semiannual (Days 8–10)	TAN-27, TAN-28, TAN-29, TAN-30A, TAN-37A, TAN-37B, TAN-D2, TAN-1860, and TAN-1861	AED Analysis Set, ^{3}H, and SP
		TAN-1859	AED Analysis Set, ^{3}H, GS, and SP
		TSF-05A, TSF-05B, TAN-31, TAN-26, TAN-37C, and TAN-10A	AED Analysis Set, ^{3}H, ^{90}Sr, GS, and SP
		TAN-25	AED Analysis Set, ^{3}H, ^{90}Sr, GS, MB, and SP
June 1, 2004	Baseline groundwater monitoring (Day 23)[b]	TSF-05A, TSF-05B, TAN-31	AED Analysis Set
		TAN-25	AED Analysis Set, MB
June 14–16, 2004	ISB sampling, monthly (Days 36–38)	TAN-27, TAN-28, TAN-29, TAN-30A, TAN-37A, TAN-37B, TAN-37C, TAN-10A, TAN-D2, TAN-1860, and TAN-1861	AED Analysis Set, ^{3}H
		TAN-1859	AED Analysis Set, ^{3}H, and GS
		TSF-05A, TSF-05B, TAN-31, and TAN-26	AED Analysis Set, ^{3}H, ^{90}Sr, and GS
		TAN-25	AED Analysis Set, ^{3}H, ^{90}Sr, GS and MB

Table 2-8. (continued).

Date(s)	Activity (Day)	Location	Analyte Set[a]
July 19–21, 2004	ISB sampling, monthly NPTF performance (Days 71–73)	TAN-27, TAN-28, TAN-29, TAN-30A, TAN-37A, TAN-37B, TAN-37C, TAN-10A, TAN-D2, TAN-1860, and TAN-1861	AED Analysis Set, ^{3}H
		TAN-1859	AED Analysis Set, ^{3}H, and GS
		TSF-05A, TSF-05B, TAN-31, and TAN-26	AED Analysis Set, ^{3}H, ^{90}Sr, and GS
		TAN-25	AED Analysis Set, ^{3}H, ^{90}Sr, GS, 9C, and MB
August 16, 2004	Whey injection #1 (Day 1)	TSF-05	NA
August 17, 2004	Groundwater monitoring (Day 2)	TSF-05A, TSF-05B, TAN-31	AED Analysis Set
		TAN-25	AED Analysis Set, MB
August 19, 2004	Groundwater monitoring (Day 4)	TSF-05A, TSF-05B, TAN-31	AED Analysis Set
		TAN-25	AED Analysis Set, MB
August 23–25, 2004	ISB sampling, quarterly (Days 8–10)	TAN-27, TAN-28, TAN-29, TAN-30A, TAN-37A, TAN-37B, TAN-37C, TAN-10A, TAN-D2, TAN-1860, and TAN-1861	AED Analysis Set, ^{3}H
		TAN-1859	AED Analysis Set, ^{3}H, and GS
		TSF-05A, TSF-05B, TAN-31, and TAN-26	AED Analysis Set, ^{3}H, ^{90}Sr, and GS
		TAN-25	AED Analysis Set, ^{3}H, ^{90}Sr, GS, and MB
September 7, 2004	Groundwater monitoring (Day 23)	TSF-05A, TSF-05B, TAN-31	AED Analysis Set
		TAN-25	AED Analysis Set, MB

Table 2-8. (continued).

Date(s)	Activity (Day)	Location	Analyte Set[a]
September 20–21, 2004	ISB sampling, monthly (Days 36–37)	TAN-27, TAN-28, TAN-29, TAN-30A, TAN-37A, TAN-37B, TAN-37C, TAN-10A, TAN-D2, TAN-1860, and TAN-1861	AED Analysis Set, ^{3}H
		TAN-1859	AED Analysis Set, ^{3}H, and GS
		TSF-05A, TSF-05B, TAN-31, and TAN-2	AED Analysis Set, ^{3}H, ^{90}Sr, and GS
		TAN-25	AED Analysis Set, ^{3}H, ^{90}Sr, GS, and MB

a. The analyte set key is provided in Table 2-9.
b. Sampling postponed 1 day due to Memorial Day Holiday.
c. Sampling postponed 1 day due to Labor Day Holiday.

AED = alternate electron donor
ISB = in situ bioremediation
NPTF = New Pump and Treat Facility

Table 2-9. Key for analyte sets shown in Table 2-8.

Analyte Set Code	Analytes
AED Analysis Set	Sodium lactate electron donor constituents (lactate, propionate, butyrate, acetate) or whey powder electron donor constituents (lactose, propionate, butyrate, acetate, isobutyrate, isovalerate, valerate, hexanoate, formate), COD, VOCs (PCE, TCE, cis-DCE, trans-DCE, VC), and dissolved gases (ethene/ethane/methane), redox indicators (sulfate, iron, pH, ORP)
MB	Microbial parameters (deoxyribonucleic acid [DNA])
^{90}Sr	Sr-90
^{3}H	Tritium
GS	Gamma screen
SP	VOC splits (off-Site lab)
9C	Research sample
NA	No samples collected

AED = alternate electron donor
COD = chemical oxygen demand
DNA = deoxyribonucleic acid
ORP = oxidation reduction potential
OVOC = volatile organic
PCE = tetrachloroethene
TCE = trichloroethene

2.4 Water Quality Instrument Monitoring

Multiparameter water quality instruments were used to collect in situ water quality data from a subset of ISB wells for the entire reporting period and to collect purge parameter data during the November and December 2003 ISB monthly sampling events. Results are reported in Section 3.3 and data are provided on the attached CD-ROM (Appendix C). Two instrument types, the Multi Parameter TROLL® 9000E (manufactured by In Situ, Inc.) and the Hydrolab® (manufactured by the Hach Company), were used to measure all or a subset of the following parameters: temperature, depth, oxidation reduction potential (ORP), pH, dissolved oxygen, and specific conductance during in situ deployment. In situ specific conductance data were used qualitatively to assess distribution of electron donor. In situ temperature, pH, and ORP data were used qualitatively to assess suitability of aquifer conditions for ARD. Operation of the water quality instruments was performed in accordance with the *ISB Operations and Maintenance Plan for Test Area North, Operable Unit 1-07B* (DOE-ID 2002b).

TROLLs® were deployed during this reporting period in Wells TAN-28 (November 2003 through September 2004), TAN-30A (November 2003 through September 2004), TAN-31 (November 2003 through September 2004), TAN-1860 (November 2003 through August 2004), TAN-1861 (November 2003 through September 2004), TAN-37A (February 2004 through September 2004) and TAN-37B (May 2004 through September 2004). TROLLs® also were used during this reporting period to collect purge parameter data during the November 2003 and December 2003 ISB monthly sampling events. Hydrolabs® were deployed in TAN-37A (from November 2003 through February 2004), TAN-37B (from November 2003 through May 2004), alternated between TAN-1859 and TSF-05 (from November 2003 through February 2004), and deployed in TAN-1859 (from March 2004 through September 2004). A CTD-Diver, manufactured by Van Essen Instruments, was deployed during this reporting period in TAN-25. The diver collects only depth, specific conductivity, and temperature data.

All multiparameter water quality instruments deployed in situ were removed for routine maintenance approximately once per month and usually redeployed the same day until January 2004 when it was determined that only ORP, depth, temperature, and specific conductance data would be collected. At this time, routine maintenance was performed approximately once every 3 months. Routine maintenance included field standardization, changing batteries, and downloading and reprogramming tests. Data gaps longer than a few days are the result of operational issues ranging from running out of battery power or malfunctioning of the instrument or the instrument probes. All operational issues for the multiparameter water quality instruments, including deployment and removal dates, are detailed in Appendix B.

2.5 Water Level Monitoring

Water levels were measured throughout the reporting period using TROLLs® (see Section 2.4), a mini TROLL® in TAN-1859, a transducer in TSF-05, and a CTD-Diver located in TAN-25. Water level data were collected every 5 minutes during electron donor injections to determine if localized water level rises (i.e., mounding) resulted. Data also were collected at 4-hour intervals between the injection periods. In addition to measuring mounding during injections, water level monitoring data were used to determine whether electron donor injections have resulted in localized changes in permeability around TSF-05. The results of water level monitoring are presented in Section 3.7.

2.6 Waste Management

As in previous years, hazardous waste was generated as a result of ISB sampling activities and managed in accordance with the requirements of the *Waste Management Plan for Test Area North Final Groundwater Remediation Operable Unit 1-07B* (INEEL 2002c). This waste included potentially contaminated wipes, sample bottles, personal protective equipment (i.e., gloves), sample residue from field analyses, sample rinsate, and purge water. Removal of all solid material and sample residue from field analyses performed in the ISB Field Laboratory was coordinated with INL Waste Generator Services. Unaltered sample rinsate and purge water was transported to the New Pump and Treat Facility (NPTF) for processing following each sampling event.

3. RESULTS

Results for the work discussed in Section 2 are presented in this section. Groundwater data are included in Appendix C (on the attached CD-ROM). Section 3.1 discusses the fate and transport of electron donor following the electron donor injections. Section 3.2 presents redox conditions, Section 3.3 evaluates the efficiency of ARD reactions, Section 3.4 discusses bioactivity indicators, and Section 3.5 evaluates the radiological monitoring data. Sections 3.6 and 3.7 present the results of water quality and water level monitoring, respectively; and quality assurance (QA) results are summarized in Section 3.8. Throughout this report, data are discussed in the following three groups:

- **Biologically Active Wells** – Wells TSF-05A, TSF-05B, TAN-25, TAN-31, and TAN-1859 are referred to as the biologically active wells because geochemical changes were observed at these monitoring locations following injections at TSF-05 and/or TAN-1859.

- **Outside Wells –** Wells TAN-37A, TAN-37B, TAN-D2, TAN-1860, TAN-1861, TAN-28, TAN-30A, TAN-29, TAN-27, and TAN-10A, which are generally considered outside the area of residual contamination, are referred to as outside wells and are located between 125 and 500 ft away from TSF-05 but were not impacted by injections at TSF-05 or TAN-1859.

- **Deep Wells –** Wells TAN-26 and TAN-37C are referred to as deep wells, as they are screened at depths greater than 300 ft and are generally characterized by extremely reducing conditions and low contaminant concentrations.

From November 2003 through February 2004, sodium lactate injections were alternated between TSF-05 and TAN-1859 and groundwater monitoring took place one week following each injection (Section 2.2). Injections of 1X 6% were performed on November 3, 2003 and January 6, 2004 into TSF-05 and on December 1, 2003 into TAN-1859. A 2X 3% injection was performed on February 9, 2004 into TAN-1859. The AED optimization was initiated in March 2004 and was conducted within the biologically active area impacted by previous electron donor injections into TSF-05. Sodium lactate injections of 1X 6% were performed on March 15, 2004 and May 10, 2004 and a 10% whey injection was performed on August 16, 2004 into TSF-05. Data collected following the two lactate injections will be used as a baseline to compare data collected following the whey powder injections into TSF-05. High-frequency groundwater monitoring included Wells TSF-05A, TSF-05B, TAN-25, and TAN-31 (the schedule is presented in Table 2-8 of this report). Day 1 is identified as the day of the injection. In general, sampling was conducted on Days 2, 4, 8–11, 22 or 23, and 36–38 following an injection (as compared to only Days 8–10 [1 week after injection] and 36–38 [5 weeks after injection] collected during normal ISB operations). In addition, data collected from TAN-1859 and TAN-37 as part of normal ISB operations were used to assess impacts from the different electron donor injections, although high-frequency sampling was not conducted at these locations. The AED optimization data are presented in this section; however, a detailed evaluation will be reported upon completion of the AED optimization in June 2005.

3.1 Electron Donor Transport and Fate

This section describes the transport and fate of electron donors following injections. The sodium lactate degradation pathway is detailed in Section 3.1.1. Development of the whey powder degradation pathway will begin following completion of the AED optimization. Data collected for determining electron donor distribution and degradation following each injection is presented in Section 3.1.2 and data collected for determining electron donor utilization is presented in Section 3.1.3.

3.1.1 Sodium Lactate Degradation Pathway

An understanding of the basis from which technical decisions have been made is necessary before a detailed description of ISB performance can take place. As stated in the *Annual Performance Report for In Situ Bioremediation Operations November 2002 to October 2003, Test Area North, Operable Unit 1-07B* (Armstrong et al. 2004), one of the important drivers for ARD is the production of hydrogen (H_2) from the fermentation of injected electron donor. Production of hydrogen from lactate proceeds via two primary pathways: the acetate pathway (Equation 3-1 [He et al. 2002]) and indirectly from the propionate pathway (Equations 3-2 [He et al. 2002] and 3-3 [Fennel and Gossett 1998]).

$$\text{lactate} + 2H_2O \rightarrow \text{acetate} + HCO_3^- + 2H_2 + 2H^+ \quad (3\text{-}1)$$

$$3\ \text{lactate} \rightarrow 2\ \text{propionate} + \text{acetate}^- + HCO_3^- + 2H^+ \quad (3\text{-}2)$$

$$\text{propionate} + 3H_2O \rightarrow \text{acetate} + HCO_3^- + 3H_2 + 3H^+ \quad (3\text{-}3)$$

Fermentation of lactate at TAN occurs via both pathways; lactate is rapidly fermented to propionate and acetate in a 3:2:1 (3 lactate to 2 propionate and 1 acetate) ratio. The propionate to acetate ratios within the biologically active wells following a lactate injection suggest that the lactate to acetate pathway is more predominant than the lactate to propionate pathway (Section 3.1.2; Figures 3-1 to 3-4). The propionate generated from lactate fermentation in Equation 3-2 can be fermented further, producing acetate, carbonate, and free hydrogen (Equation 3-3). Fermentation of propionate provides a longer-lived source of hydrogen than does lactate fermentation to acetate and hydrogen. Under extremely reducing conditions, acetate can be further oxidized to carbonate and hydrogen, via Equation 3-4 (He et al. 2002):

$$\text{acetate} + 4H_2O \rightarrow 2HCO_3 + 4H_2 + H^+ \quad (3\text{-}4)$$

Generation of hydrogen via the propionate and acetate pathways (Equations 3-3 and 3-4) is self-limiting because in order for these reactions to be energetically favorable, they require very low partial pressures of hydrogen (hydrogen accumulation) in the system (He et al. 2002). This suggests that these pathways will produce relatively low levels of hydrogen sustained over a longer period of time. The observed hydrogen accumulation (low partial pressures) in TAN groundwater suggests that hydrogenotrophic activity (i.e. methanogenesis) is repressed and that a greater fraction of hydrogen produced from the reactions shown in Equations 3-3 and 3-4 would be used by dechlorinators (Fennell, Gossett, and Zinder 1997). Recent data collected suggests that the methanogenesis activity occurring at TAN appears to be dominated by the acetoclastic (acetate-utilizing) pathway rather than the hydrogenotrophic pathway. Acetoclastic degradation produces methane and carbon dioxide, not hydrogen, which would drive ARD.

3.1.2 Electron Donor Distribution and Degradation

This section describes the distribution and degradation of electron donor following each injection event. Data contained in Figures 3-1 through 3-6 and Tables 3-1 through 3-3 show relative concentrations of electron donor at each monitoring well location within the biologically active area, which is used to indicate the donor distribution. In addition, the tables and figures show the degradation of the injected donor, as show by the accumulation and depletion of daughter products, such as propionate and acetate, during an injection cycle for both injection locations (TSF-05 and TAN-1859).

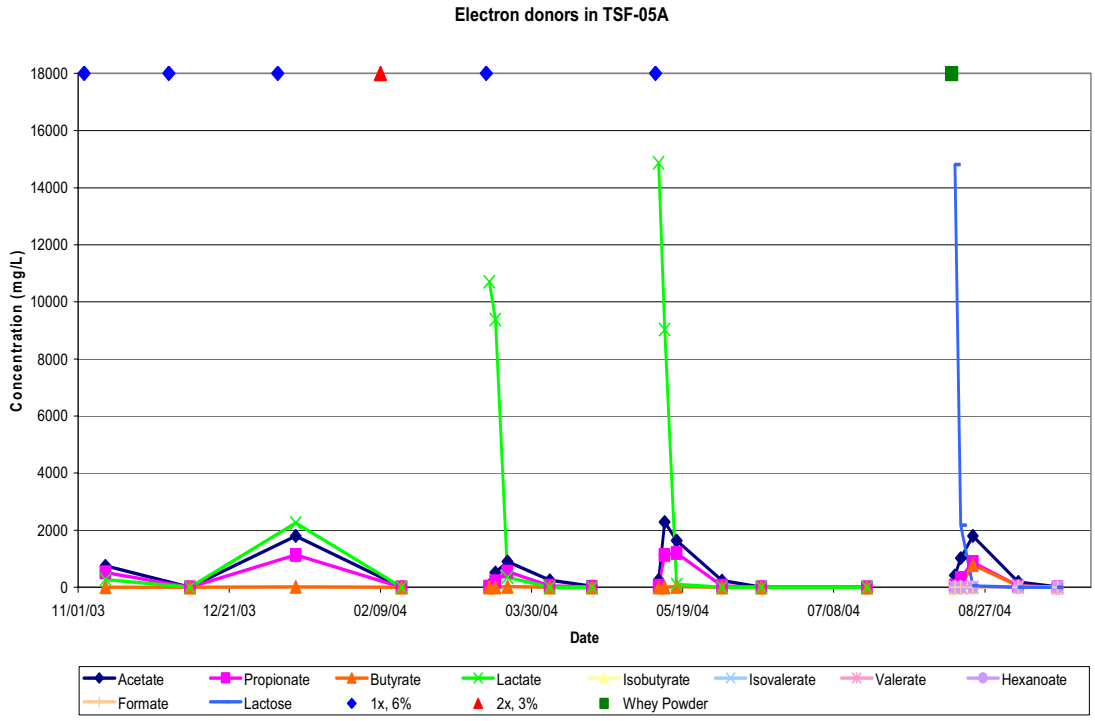

Figure 3-1. Electron donors at Well TSF-05A.

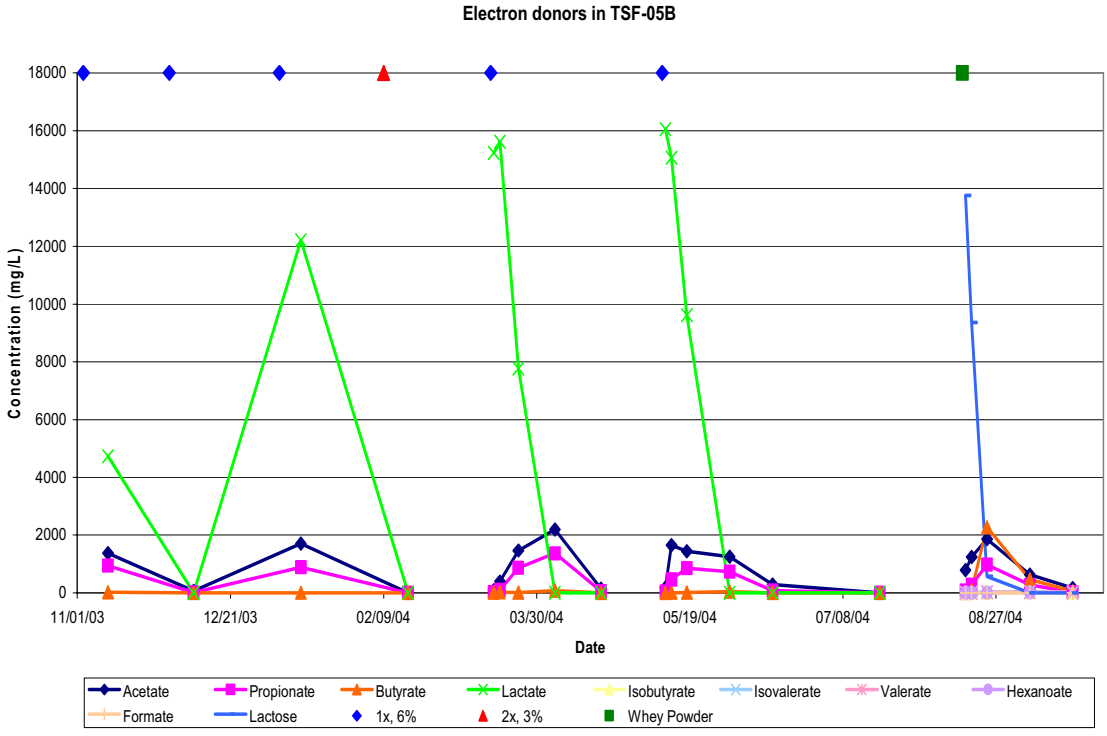

Figure 3-2. Electron donors at Well TSF-05B.

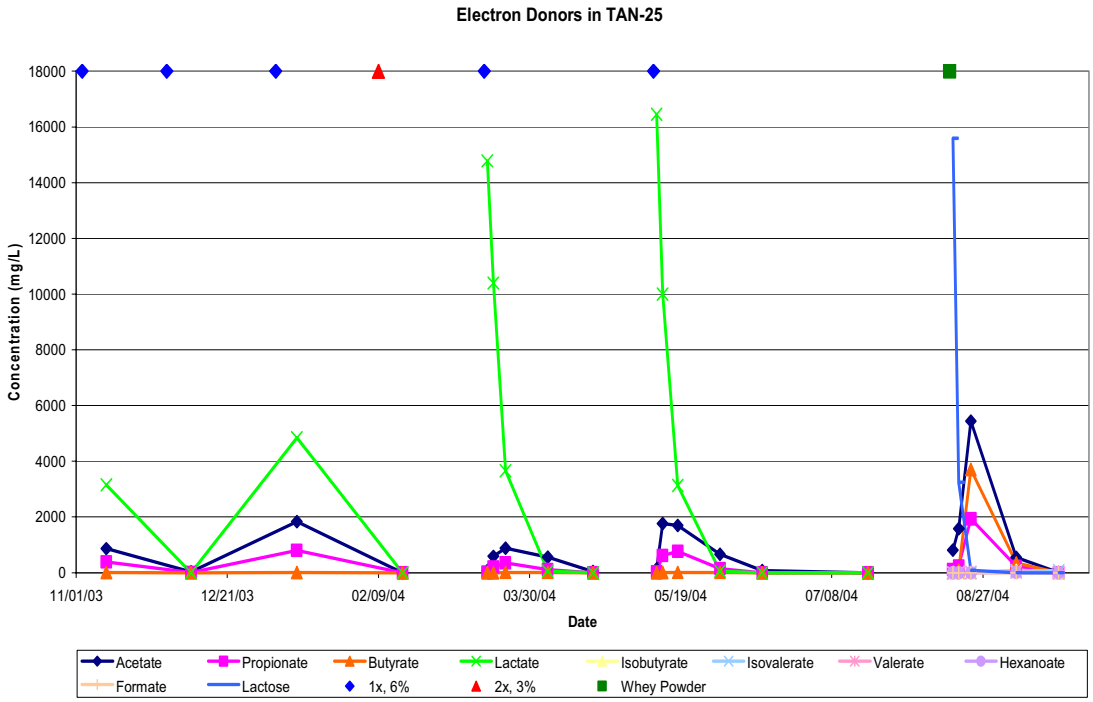

Figure 3-3. Electron donors at Well TAN-25.

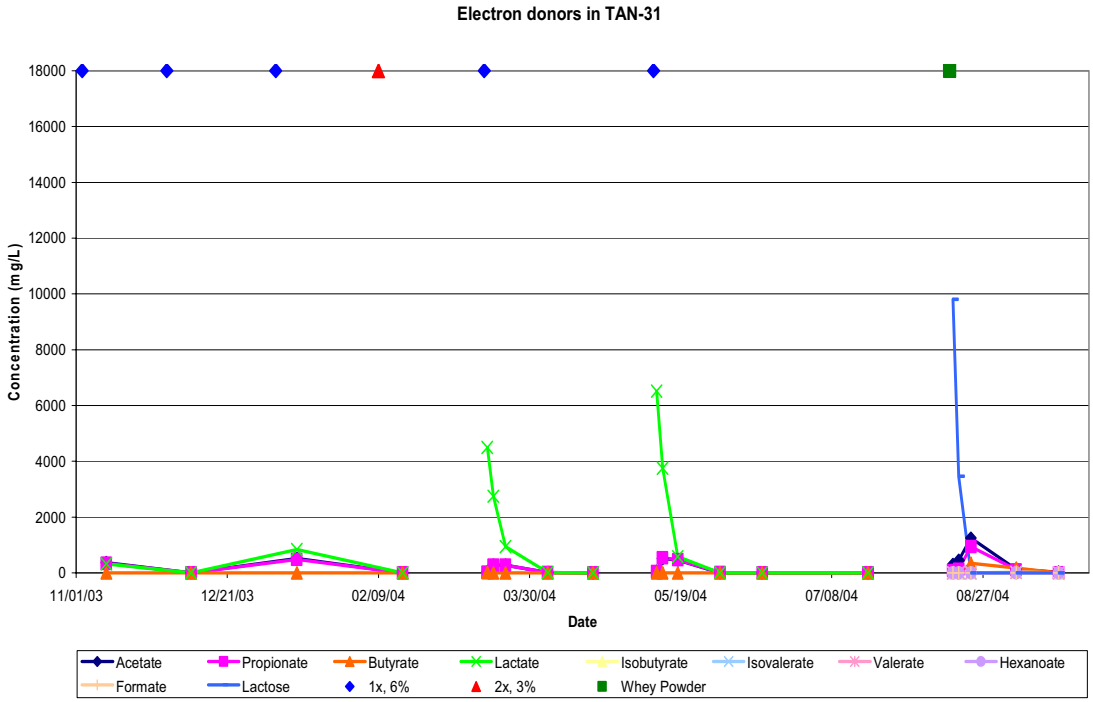

Figure 3-4. Electron donors at Well TAN-31.

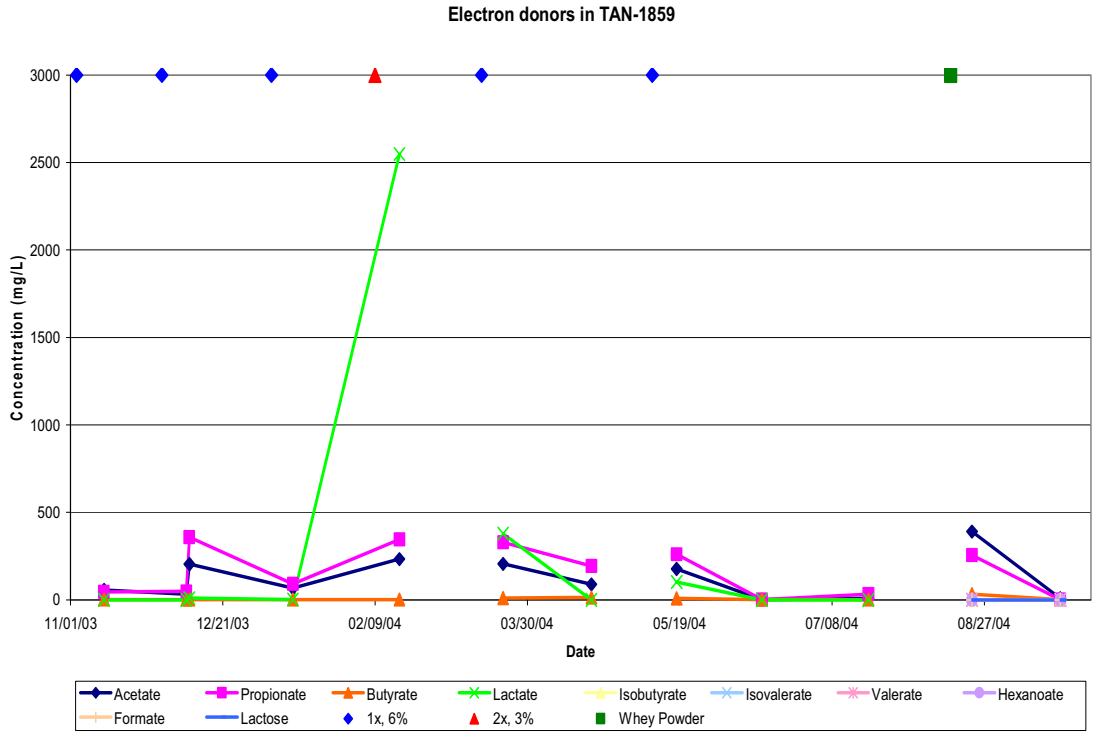

Figure 3-5. Electron donors at Well TAN-1859.

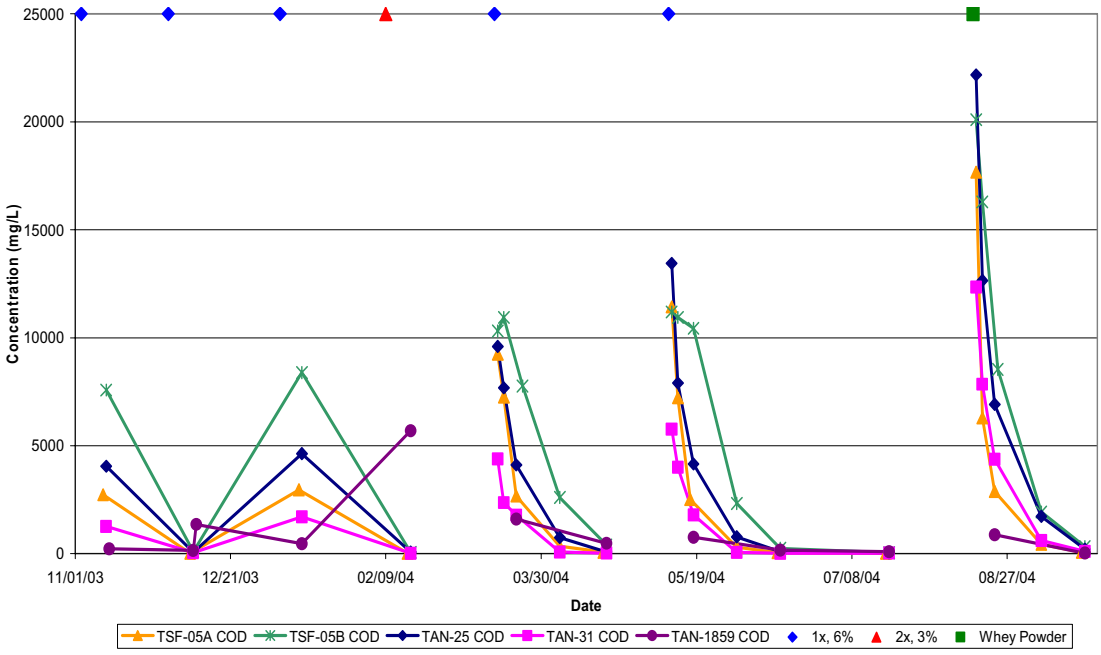

Figure 3-6. Chemical oxygen demand in the biologically active area.

Table 3-1. Electron donor data for the 1X 6% sodium lactate injection on November 3, 2003, in Well TSF-05.

Well	Time Elapsed After Injection (Days) [a]	COD (mg/L)	Lactate (mg/L) Molar %[b]	Propionate (mg/L) Molar %[b]	Acetate (mg/L) Molar %[b]	Propionate:Acetate (molar)
TSF-05A	8	2,742	279 14%	522 31%	753 55%	0.56
TSF-05A	36	17	0 [c] N/A	0 [d] N/A	10 N/A	N/A
TSF-05B	9	7,578	4,727 59%	946 14%	1,377 26%	0.56
TSF-05B	37	95	0 [c] N/A	17 N/A	72 N/A	N/A
TAN-25	9	4,050	3,150 64%	391 10%	865 26%	0.37
TAN-25	37	64	0 [c] N/A	6 N/A	34 N/A	N/A
TAN-31	9	1,266	321 25%	345 32%	369 43%	0.76
TAN-31	37	45	0 [c] N/A	8 N/A	7 N/A	N/A
TAN-1859	10	221	0 [c] 0%	46 39%	56 59%	N/A

a. Time elapsed after the day of injection. The injection day is counted as Day 1.

b. Molar percentages are only reported if the total electron donor concentrations were above 100 mg/L for a given sampling event.

c. These values were reported as <0.223, which means that lactate was detected but was below the method detection limit (MDL). These values are therefore reported here as 0 mg/L.

d. Value reported as <5 mg/L, which means that the volatile fatty acid (VFA) was detected but was below the MDL. These values are reported here as 0 mg/L.

Table 3-2. Electron donor data for the 1X 6% sodium lactate injection on January 6, 2004, in Well TSF-05.

Well	Time Elapsed After Injection (Days) [a]	COD (mg/L)	Lactate (mg/L) Molar % [b]	Propionate (mg/L) Molar % [b]	Acetate (mg/L) Molar % [b]	Propionate:Acetate (molar)
TSF-05A	7	2,961	2,253 35%	1,137 22%	1,799 43%	0.51
TSF-05A	42	18	0 [c] N/A	0 [d] N/A	6.3 N/A	N/A
TSF-05B	8	8,388	12,212 77%	888 7%	1,703 16%	0.42
TSF-05B	43	68	0 [c] N/A	0 [d] N/A	0 [d] N/A	N/A
TAN-25	8	4,635	4,850 56%	796 11%	1,834 32%	0.35
TAN-25	43	75	0 [c] N/A	0 [d] N/A	0 [d] N/A	N/A
TAN-31	8	1700	840 38%	487 27%	517 35%	0.76
TAN-31	43	19	0 [c] N/A	0 [d] N/A	6 N/A	N/A
TAN-1859	8	464	2 N/A	91 N/A	67 N/A	N/A

a. Time elapsed after the day of injection. The injection day is counted as Day 1.

b. Molar percentages are only reported if the total electron donor concentration was above 100 mg/L for a given sampling event. If less than 100 mg/L, N/A is reported.

c. These values were reported as <0.223, which means that lactate was detected but was below the MDL. These values are therefore reported here as 0 mg/L.

d. Value reported as <5 mg/L, which means that the volatile fatty acid was detected but was below the MDL. These values are therefore reported here as 0 mg/L.

Table 3-3. Electron donor data for the 1X 6% sodium lactate injections in Well TAN-1859.

Well	Injection Date	Time Elapsed After Injection (Days) [a]	COD (mg/L)	Lactate (mg/L) Molar % [b]	Propionate (mg/L) Molar % [b]	Acetate (mg/L) Molar % [b]	Propionate: Acetate (molar)
TAN-1859	December 1, 2003	10	1,359	9.507 N/A	358.2 53%	204.8 45%	1.41
TAN-1859	February 8-9, 2004	8	5,697	2,548.5 77%	345.9 13%	233.0 11%	1.20

a. Time elapsed after the day of injection. The injection day is counted as Day 1.

b. Molar percentages are only reported if the total electron donor concentrations were above 100 mg/L for a given sampling event.

Concentrations of lactate, acetate, propionate, butyrate, and additional volatile fatty acids (VFAs) (following whey injections) were measured. For the charts and tables created to show the mass and moles of these constituents for each monitoring location, it should be noted that the molar percentages may not sum to 100% because butyrate was omitted following sodium lactate injections since it generally comprised less than 1% of the total moles of electron donor. The COD also was measured as an indicator of total electron donor. The electron donor mass charts for all wells are presented in Appendix C (see attached CD-ROM).

3.1.2.1 Biologically Active Wells - TSF-05 Injections (November 2003 and January 2004). Electron donor distribution for 1X 6% injections in TSF-05 was similar to past 1X 6% injections, with donor observed at TSF-05A, TSF-05B, TAN-25, TAN-31, and TAN-1859. No electron donor was observed at any other monitoring locations. Following each injection, electron donor concentrations were highest at TSF-05B (COD at approximately 8,000 mg/L), followed by concentrations at TAN-25, TSF-05A, and TAN-31 (COD at approximately 4,500 mg/L, 3,000 mg/L, and 1,500 mg/L, respectively) one week following an injection (Tables 3-1 and 3-2, and Figures 3-1 through 3-4). Electron donor also was distributed to TAN-1859, as indicated by COD concentrations greater than 100 mg/L measured one week following injection at TSF-05 (Figure 3-5).

Sodium lactate was fermented to propionate and acetate following the injections into TSF-05 (Tables 3-1 and 3-2). The week following the November 2003 injection, propionate and acetate concentrations were high in TSF-05A (522 and 753 mg/L), TSF-05B (946 and 1377 mg/L), TAN-25 (391 and 865 mg/L), and TAN-31 (345 and 369 mg/L). The resultant propionate to acetate molar ratio was 0.56 in TSF-05A and TSF-05B, 0.37 in TAN-25, and 0.76 in TAN-31. The analytical results one week following the January 2004 sodium lactate injection were similar to the November 2003 injection as was the propionate to acetate ratio (TSF-05A 0.51, TSF-05B 0.42, TAN-25 0.35, and TAN-31 0.76).

3.1.2.2 Biologically Active Wells - TAN-1859 Injections (December 2003 and February 2004). Well TAN-1859, which is a new injection location downgradient from Well TSF-05, was constructed to deliver electron donor to locations within the residual source area not impacted by TSF-05 injections. The first injection at this location occurred December 1, 2003 at 1X 6%. Sampling at Well TAN-1859 was performed 9 days after the injection (on December 9, 2003), at a depth of 218 ft. The concentration of COD at this depth was 150 mg/L, which is very low when compared with COD concentrations of 8,000 mg/L measured at TSF-05B, 8 to 9 days following injection in TSF-05 (Table 3-3). The injection line in TAN-1859 is screened from 210 ft below land surface (bls) to 270 ft bls. Therefore, a decision was made to lower the pump to 245 ft bls in order to determine if the electron donor was being transported vertically within the well. Additional samples were collected from this depth 10 days after injection (on December 10, 2003), which confirmed (COD of 1,359 mg/L) that significant vertical transport of the electron donor solution had occurred in this well. Based on these data, the decision was made to keep the sampling depth of TAN-1859 at 245 ft bls for the remainder of the reporting period. Electron donor was not observed at any other monitoring location following injection into TAN-1859.

A second injection was performed into TAN-1859 on February 9, 2004. This injection was a 2X 3% (approximately 24,000 gal, 3% nominal concentration) lactate injection. The concentration of lactate was decreased to 3% in order to minimize the vertical transport and increase the lateral distribution of electron donor within the target zone of the TAN aquifer. Sampling at this location 9 days after the injection revealed the COD concentration to be much higher (5,697 mg/L) following this injection than in the previous injection (Table 3-4 and Figure 3-5). Following this second injection at TAN-1859, detectable concentrations of electron donor, as determined by COD, were only observed in the injection well (TAN-1859). All of the biologically active wells were sampled and no increase in electron donor concentration was observed. Therefore, the extent of lateral electron donor transport is unknown.

Table 3-4. Electron donor data for the 1X 6% sodium lactate injection on March 15, 2004 in Well TSF-05.

Well	Sampling Event (Day)	COD (mg/L)	Lactate (mg/L) Molar %	Propionate (mg/L) Molar %	Acetate (mg/L) Molar %	Butyrate (mg/L) Molar (%)	Propionate: Acetate (molar)
TSF-05A	2	9,200	10,700 99%	21 [b] 0%	69 1%	0 [c] 0%	0.24
TSF-05A	4	7,300	9,400 90%	206 2%	514 8%	0 [c] 0%	0.32
TSF-05A	8	2,700	350 14%	550 28%	905 57%	21 1%	0.49
TSF-05A	22	350	0 [a] 0%	50 14%	240 85%	0 [c] 0%	0.16
TSF-05A	36	75	0 [a] 0%	12 20%	36 77%	0 [c] 3%	0.26
TSF-05B	2	10,300	15,200 99%	24 [b] 0%	95 1%	19 [b] 0%	0.21
TSF-05B	4	10,900	15,600 95%	102 1%	400 4%	21 [b] 0%	0.21
TSF-05B	10	7,767	7,800 70%	870 10%	1,500 20%	15 [b] 0%	0.48
TSF-05B	22	2,610	2 [b] 0%	1,400 33%	2,200 65%	77 2%	0.51
TSF-05B	37	400	0 [a] 0%	56 24%	144 75%	0 [c] 0%	0.31
TAN-25	2	9,600	14,800 99%	24[b] 0%	82 1%	0 [c] 0%	0.24
TAN-25	4	7,700	10,400 90%	203 2%	590 8%	0 [c] 0%	0.28
TAN-25	8	4,100	3,700 67%	360 8%	885 25%	13 [b] 0%	0.33
TAN-25	22	740	50 5%	112 13%	560 81%	17 1%	0.16
TAN-25	37	82	0 [a] 0%	0 [a] 0%	46 100%	0 [c] 0%	0.04
TAN-31	2	4,400	4,500 98%	23 1%	36 1%	19 [b] 0%	0.52
TAN-31	4	2,400	2,800 78%	280 10%	275 12%	0 [c] 0%	0.83
TAN-31	10	1,800	940 55%	270 20%	290 25%	0 [c] 0%	0.79

Table 3-4. (continued).

Well	Sampling Event (Day)	COD (mg/L)	Lactate (mg/L) Molar %	Propionate (mg/L) Molar %	Acetate (mg/L) Molar %	Butyrate (mg/L) Molar (%)	Propionate: Acetate (molar)
TAN-31	22	77	15 24%	16 32%	18 44%	0 [c] 0%	0.72
TAN-31	37	28	0 [a] 0%	0 [c] 0%	0 [c] 0%	0 [c] 0%	0.81
TAN-1859	8	1,600	380 35%	330 36%	206 28%	11 1%	1.29
TAN-1859	37	480	0 [a] 0%	200 61%	90 35%	13 4%	1.76

a. These values were reported as <0.223, which means that lactate was detected but was below the MDL. These values are therefore reported here as 0 mg/L.

b. Although there are VFAs present, when the molar percentage was calculated, the percent of the VFA was so small that 0% was recorded.

c. Value reported as <5 mg/L, which means that the VFA was detected but was below the MDL. These values are therefore reported here as 0 mg/L.

December 10, 2003 VFA results from TAN-1859, 10 days following the 1X 6% injection, suggest that by this time lactate was significantly depleted (9.5 mg/L) with complete conversion to propionate (358 mg/L) and acetate (205 mg/L) (Tables 3-3 and 3-4). The samples collected 8 days after the February 2004 2X 3% injection suggest high concentrations of VFAs, with lactate at 2549 mg/L, propionate at 346 mg/L and acetate at 233 mg/L. The propionate to acetate ratio was higher in TAN-1859 (1.41 and 1.20) following the December 2003 and February 2004 injections, as compared to TSF-05 following the November 2003 (0.56) and January 2004 (0.42 to 0.51) injections.

3.1.2.3 Biologically Active Wells - AED Optimization Sodium Lactate Injections in Well TSF-05 (March 2004 and May 2004). Sodium lactate injections of 1X 6% with high-frequency sampling were performed March 15, 2004, and May 10, 2005. On Days 2 and 4 following the first sodium lactate injection (March 15, 2004), lactate and COD concentrations were the highest ever observed at TSF-05B (15,200 and 10,300 mg/L), TAN-25 (14,800 and 9,600 mg/L), TSF-05A (10,700 and 9,200 mg/L), and TAN-31 (4,500 and 4,400 mg/L; Table 3-4). Figure 3-6 shows the COD concentration versus time for all AED wells, and Figures 3-1 through 3-5 show electron donor molar concentrations versus time. After the second 1X 6% AED optimization sodium lactate injection on May 10, 2005, lactate and COD concentrations were generally higher than those observed after the first sodium lactate injection. Lactate and COD concentrations were the highest in TAN-25 (16,500 and 13,500 mg/L, respectively), followed by TSF-05B (16,000 and 11,200 mg/L, respectively), TSF-05A (14,900 and 11,400 mg/L, respectively), and then TAN-31 (6,500 and 5,800 mg/L, respectively; Table 3-5).

As shown in Tables 3-4 and 3-5, the week following the injection (Days 8–10), propionate and acetate concentrations were the highest observed over the injection cycle at TSF-05A (550 and 905 mg/L), TSF-05B (870 and 1,500 mg/L), TAN-25 (360 and 885 mg/L), and TAN-31 (270 and 290 mg/L). Lactate concentrations were higher than propionate and acetate at TSF-05B (7,800 mg/L), TAN-25 (3,700 mg/L), and TAN-31 (940 mg/L), and lower at TSF-05A (350 mg/L) by Days 8–10. By Day 22 or 23, lactate was depleted in TSF-05A and TSF-05B and significantly reduced at TAN-25 (740 mg/L) and TAN-31 (15 mg/L) and by Days 36–38, only propionate and acetate were present at TSF-05A (12 and 36 mg/L) and TSF-05B (56 and 144 mg/L) and only acetate was present at TAN-25 (46 mg/L). All electron donors were gone by Days 36–38 at TAN-31.

Table 3-5. Electron donor data for the 1X 6% sodium lactate injection on May 10, 2004 in Well TSF-05.

Well	Time Elapsed After Injection (Days)	COD (mg/L)	Lactate (mg/L) Molar %	Propionate (mg/L) Molar %	Acetate (mg/L) Molar %	Butyrate (mg/L) Molar (%)	Propionate: Acetate (molar)
TSF-05A	2	11,400	14,900 97%	59 1%	258 2%	0 [c] N/A	0.19
TSF-05A	4	7,200	9,000 65%	1,100 10%	2,300 25%	0 [c] 0%	0.40
TSF-05A	8	2,500	105 3%	1,200 36%	1,600 61%	22[b] 0%	0.59
TSF-05A	23	295	1 [b] 0%	54 15%	241 84%	0 [c] 0%	0.18
TSF-05A	36	56	0 [a] 0%	0 [c] 0%	0 [c] 0%	0 [c] 0%	0.81
TSF-05A	71	19	0 [a] 0%	0 [c] 0%	0 [c] 0%	0 [c] 0%	0.81
TSF-05B	2	11,200	16,000 98%	43 [b] 0%	185 2%	0 [c] 0%	0.19
TSF-05B	4	10,900	15,000 83%	467.7 3%	1,653.8 14%	9 [b] 0%	0.23
TSF-05B	9	10,400	9,600 75%	860 8%	1,400 17%	12 [b] 0%	0.48
TSF-05B	23	2,300	0 [a] 0%	730 31%	1,300 67%	46 2%	0.47
TSF-05B	37	251	0 [a] 0%	78 18%	287 82%	0 [c] 0%	0.22
TSF-05B	72	44	0 [a] 0%	0 [c] 0%	0 [c] 0%	0 [c] 0%	0.81
TAN-25	2	13,500	16,500 99%	34 [b] 0%	137 1%	0 [c] 0%	0.20
TAN-25	4	7,900	10,000 74%	617 6%	1,800 20%	6 [b] 0%	0.28
TAN-25	9	4,100	3,100 47%	770 14%	1,700 39%	16 1%	0.37
TAN-25	23	781	63 5%	150 14%	663 80%	13 1%	0.18
TAN-25	37	103	0 [a] 0%	0 [c] 0%	73 100%	0 [c] 0%	0.03
TAN-25	72	36	0 [a] 0%	0 [c] 0%	0 [c] 0%	0 [c] 0%	0.81
TAN-31	2	5,800	6,500 98%	46 1%	65 1%	0 [c] 0%	0.57
TAN-31	4	4,000	3,800 72%	550 13%	520 15%	0 [c] 0%	0.85

Table 3-5. (continued).

Well	Time Elapsed After Injection (Days)	COD (mg/L)	Lactate (mg/L) Molar %	Propionate (mg/L) Molar %	Acetate (mg/L) Molar %	Butyrate (mg/L) Molar (%)	Propionate: Acetate (molar)
TAN-31	9	1,800	580 31%	480 31%	461 37%	0 [c] 0%	0.84
TAN-31	23	66	4 24%	13 76%	0 [c] 0%	0 [c] 0%	4.30
TAN-31	37	23	0 [a] 0%	0 [c] 0%	0 [c] 0%	0 [c] 0%	0.81
TAN-31	72	26.5	0 [a] 0%	0 [c] 0%	0 [c] 0%	0 [c] 0%	0.81
TAN-1859	9	759	103 15%	261 46%	180 38%	9 1%	1.19
TAN-1859	37	168	0 [a] 0%	0 [c] 0%	0 [c] 0%	0 [c] 0%	0.81
TAN-1859	72	95	0 [a] 0%	33 79%	9 21%	0 [c] 0%	2.99

a. These values were reported as <0.223, which means that lactate was detected, but below the MDL. These values are therefore reported here as 0 mg/L.

b. Although lactate or butyrate was present, when the molar percentage was calculated the percent lactate was so small that 0% was recorded.

c. Value reported as <5 mg/L, which means that the VFA was detected, but below the MDL. These values are therefore reported here as 0 mg/L.

Electron donor also was distributed to TAN-1859, about 90 ft downgradient of the injection well (TSF-05). Approximately 1 week after the first sodium lactate injection, TAN-1859 had COD and lactate concentrations of 1,600 and 380 mg/L, respectively, and 1 week after the second sodium lactate injection, concentrations of 760 and 103 mg/L were observed. The higher COD concentration observed following the first lactate injection was likely a residual effect of the lactate injection at TAN-1859 on February 9, 2004. It is likely that electron donor was still present at TAN-1859 up to and including the start of the AED optimization (March 2004).

For the AED optimization, a detailed description of the degradation of lactate into daughter products is presented. Tables 3-4 and 3-5 illustrate the molar percentages of the VFAs for the biologically active wells. The mole fractions of lactate, propionate, and acetate illustrate the conversion of lactate to propionate and acetate, and then from propionate to acetate. The day after injection, all electron donor was present as lactate (98 to 99%) in all of the AED wells. However, by Days 8–10 propionate and acetate production was evident by increasing mole percentages at TSF-05A (28 and 57%), TSF-05B (10 and 20%), TAN-25 (8 and 25%) and TAN-31 (20 and 25%). Lactate remained the major VFA at TSF-05B and TAN-25 (70 and 67%) at Days 8–10. By Day 22 or 23, lactate was no longer found at TSF-05A and TSF-05B and propionate and acetate comprised the majority of the electron donors with mole percentages of 14 and 85% in TSF-05A and 33 and 65% in TSF-05B. TAN-25 had low concentrations of lactate (50 mg/L and 5% mole percentage) but much higher propionate (112 mg/L and 13% mole percentage) and acetate (560 mg/L and 81% mole percentage). TAN-31 was significantly depleted of electron donor by Days 22–23. By Days 36–38, the electron donor continued to be depleted at TSF-05A and TSF-05B, with the relative fractions of propionate and acetate similar to the Day 22 or 23 sampling event. TAN-25 had only low concentrations of acetate (46 mg/L) and TAN-31 had no electron donor. The accumulation of propionate and acetate is also tracked using the propionate to acetate ratio (Table 3-4 and 3-5). The propionate to acetate ratio was highest for all of the well locations except

TAN-31 and TAN-1859 on Day 8 following the March 2004 injection. This ratio then subsequently declines as propionate is degraded to acetate.

The electron donor distribution following the May 2004 sodium lactate injection was very similar to the response following the March 2004 injection at the AED well locations. The conversion of lactate to propionate and acetate also was efficient, as suggested by generation of significant amounts of propionate and acetate 1 week following the injection at TSF-05A (1,200 and 1,600 mg/L), TSF-05B (860 and 1,400 mg/L), TAN-25 (770 and 1,700 mg/L), and TAN-31 (480 and 461 mg/L). By the Day 22 or 23 sampling event, acetate was the major VFA remaining, with concentrations and molar percentages at 241 mg/L and 84% at TSF-05A, 1,300 mg/L and 67% at TSF-05B, and 663 mg/L and 80% at TAN-25. Electron donor was depleted in TAN-31 at the Day 22 or 23 sampling event. No electron donor remained at TSF-05A and TAN-31 by the Days 36–38 sampling event; 78 mg/L propionate and 287 mg/L acetate were present at TSF-05B and 73 mg/L acetate was present at TAN-25. At the Days 71–73 sampling event, no electron donor was present at any of the AED wells. The trend of the propionate to acetate ratio is similar following the May 2004 injection as was observed following the March 2004 injection. The ratio was highest at the AED well locations, except for TAN-31, 8 days after the injection as lactate was fermented to propionate and acetate, and then subsequently declined as propionate was converted to acetate.

Well TAN-1859 also was used to estimate the electron donor distribution during the AED optimization, although this well was only sampled during regular ISB sampling events (Tables 3-4 and 3-5). It was sampled on Days 8–10 and 36–38 after each lactate injection, and then an additional sampling event occurred on Days 71–73 after the second lactate injection. The week after the March 2004 sodium lactate injection, lactate concentrations were 380 mg/L, propionate concentrations were 330 mg/L, and acetate concentrations were 206 mg/L. By the Days 36–38 sampling event, the lactate concentration was nondetect with propionate at 200 mg/L and acetate at 90 mg/L. One week after the May 2004 lactate injection, lactate concentrations at TAN-1859 were 103 mg/L, propionate concentrations were 261 mg/L, and acetate concentrations were 180 mg/L. By Days 36–38 following the second lactate injection, lactate, propionate, and acetate were all nondetect. On Days 71–73 after the second lactate injection, propionate and acetate were detected with concentrations at 33 and 9 mg/L. As observed following the November 2003 and January 2004 sodium lactate injections into TSF-05, the propionate to acetate ratio at TAN-1859 following the March 2004 injection was higher 8 days after injection than observed for any of the AED well locations.

3.1.2.4 Biologically Active Wells - AED Optimization Whey Injection in Well TSF-05 (August 2004). The first whey powder injection was performed in TSF-05 on August 16, 2004. The dominant electron donor observed immediately after the injection (Day 2 and 4) was lactose. The major electron donors observed in the AED wells during the sampling cycle following the whey powder injection were lactose, acetate, propionate, and butyrate. Minor products included isobutyrate, isovalerate, valerate, and hexanoate. Formate was nondetect in every AED well. The concentrations of electron donors and the molar percentages of each VFA in relation to the total VFA concentrations in the electron donor-impacted wells following the first whey powder injection can be seen in Table 3-6.

The injection concentration of whey powder was higher than sodium lactate (10% vs. 6%). Consequently, COD concentrations at the AED wells were much higher following the whey powder injection (20,000 mg/L in TSF-05B) than COD concentrations observed after the sodium lactate injections (10,000 to 11,000 mg/L in TSF-05B). Higher concentrations of COD also were observed at TSF-05A (17,700 vs. 9,000 to 11,000 mg/L), TAN-25 (22,000 vs. 13,000 mg/L), and TAN-31 (12,000 vs. 5,800 mg/L) the day after injection. The COD concentrations at TAN-1859 were approximately 880 mg/L after the whey powder injection, which is slightly higher than the COD concentrations (760 mg/L)

observed at this well after the May 2004 sodium lactate injection. Electron donor, however, was not distributed to TAN-37A or TAN-37B.

Whey powder is comprised of approximately 70% w/w lactose. Therefore, high concentrations of lactose were observed at TAN-25 (15,600 mg/L), TSF-05A (14,800 mg/L), TSF-05B (13,800 mg/L), and TAN-31 (9,800 mg/L) the day after the whey powder injection (Day 2) (Table 3-6). By the Day 4 sampling event, lactose concentrations significantly declined at TSF-05B (9,400 mg/L), TAN-25 (3,200 mg/L), TAN-31 (3,500 mg/L), and TSF-05A (2,200 mg/L) following the whey powder injection. By the Days 8–10 sampling event, lactose concentrations were depleted at all monitoring locations except for TSF-05B (~500 mg/L).

The week following the injection (Days 8–10), propionate, acetate, and butyrate were the primary daughter products observed from lactose degradation with high concentrations of each observed at TSF 05A (880, 1800 and 784 mg/L), TSF-05B (980, 1,900, and 2,300 mg/L), TAN-25 (1,900, 5,400, 3,700 mg/L), and TAN-31 (940, 1,250, 346 mg/L). By the Day 23 sampling event, propionate, acetate, and butyrate concentrations had declined at all of the sampling locations, but trace amounts (7–86 mg/L) of isobutyrate, isovalerate, valerate and hexanoate were detected. The electron donors were further depleted by the Days 36–38 sampling event with acetate and isovalerate present at TSF-05A (16 and 16 mg/L), with propionate (22 mg/L), acetate (170 mg/L), butyrate (54 mg/L, isobutyrate (14 mg/L), valerate (20 mg/L), and hexanoate (17 mg/L) present at TSF-05B, with isobutyrate (2 mg/L) and isovalerate (76 mg/L) present at TAN-25, and with propionate (8 mg/L), acetate (21 mg/L), butyrate (4 mg/L), and isobutyrate (2 mg/L) present at TAN-31. Electron donor also was distributed to TAN-1859, about 90 ft downgradient of the injection well (TSF-05) following the whey powder injection. Approximately 1 week after the injection, TAN-1859 had COD concentrations of 880 mg/L. By Day 8, no lactose was detected at TAN-1859, but propionate (260 mg/L), acetate (390 mg/L) and butyrate (32 mg/L) were detected. Only low concentrations of acetate (8 mg/L) were detected at TAN-1859 by the Day 37 sampling event. The molar fractions of the different VFAs generated from whey powder degradation are presented in Table 3-7, but will not be discussed until the AED optimization is complete and additional whey injections have been evaluated.

3.1.2.5 Outside and Deep Wells - All Injections.

As observed in previous reporting periods, electron donor injection into TSF-05 did not impact any of the outside or deep locations. This trend continued during this reporting period, with no distribution of electron donor to any of the outside or deep locations. Likewise, injections into TAN-1859 did not distribute electron donor to any other monitoring location, including TAN-37A or TAN-37B.

3.1.3 Electron Donor Utilization

Electron donor utilization rate in relation to the rate of contaminant degradation is an important factor in optimizing ISB operations at TAN. One goal of optimization is to minimize the number of times electron donor is injected, while at the same time maximizing enhanced dissolution of the residual source and stimulating high dechlorination rates.

3.1.3.1 Routine Sodium Lactate Injections (November 2003 through February 2004).

During lactate injections, concentrations of electron donor are evaluated by measuring COD, lactate, propionate, butyrate, and acetate. Past data suggest that COD is roughly equivalent to the sum of lactate and the fermentation products. Concentration changes for each parameter following each injection provide information relating to the utilization rate of the injected electron donor solution. For example, Figure 3-7 illustrates the decline in COD concentrations over an approximately 1-month period following each injection.

Table 3-6. Electron donor data for the August 16, 2004 whey powder injection in Well TSF-05.

Well	Time Elapsed After Injection (Days)	COD (mg/L)	Lactose (mg/L) Molar %	Propionate (mg/L) Molar %	Acetate (mg/L) Molar %	Butyrate (mg/L) Molar (%)	Isobutyrate (mg/L) Molar %	Isovalerate (mg/L) Molar %	Valerate (mg/L) Molar %	Hexanoate (mg/L) Molar %
TSF-05A	2	17,700	14,800 84%	59 2%	420 14%	0 [a] 0%	0 [a] 0%	0 [a] 0%	0 0%	0 0%
TSF-05A	4	6,300	2,200 22%	331.2 16%	1,000 60%	33 1%	0 [a] 0%	0 [a] 0%	0 0%	0 0%
TSF-05A	8	2,900	0 [b] 0%	880 23%	1,800 59%	784 17%	0 [a] 0%	0 [a] 0%	0 0%	0 0%
TSF-05A	23	441	0 [b] 3%	44 12%	186 62%	50 11%	25 6%	28 5%	7 1%	0 0%
TSF-05A	36	66	0 0%	0 [a] 0%	16 49%	0 [a] 0%	0 [a] 0%	16 29%	0 [a] 0%	0 0%
TSF-05B	2	20,000	13,800 74%	80 2%	780 24%	0 [a] 0%	0 [a] 0%	0 [a] 0%	0 0%	0 0%
TSF-05B	4	16,300	9,400 51%	280 7%	1,245 39%	107 2%	0 [a] 0%	0 [a] 0%	0 0%	0 0%
TSF-05B	9	8,500	567 2%	980 19%	1,900 44%	2,300 36%	11 0%	33 [a]0%	23 [a]0%	0 0%
TSF-05B	23	1,900	0 [b] 0%	280 7%	630 66%	470 14%	41 4%	38 1%	23 5%	8 3%
TSF-05B	37	322	0 0%	22 7%	170 66%	54 14%	14 4%	0 [a] 0%	20 5%	17 3%
TAN-25	2	22,000	15,600 75%	120 3%	813 23%	0 [a] 0%	0 [a] 0%	0 [a] 0%	0 0%	0 0%
TAN-25	4	12,700	3,200 23%	240 8%	1,600 65%	105 3%	9 [a]0%	20 [a]0%	0 0%	0 0%
TAN-25	9	6,900	0[b] 0%	1,900 16%	5,400 57%	3,700 26%	7 [a]0%	21 [a]0%	0%	0%

Table 3-6. (continued).

Well	Time Elapsed After Injection (Days)	COD (mg/L)	Lactose (mg/L) Molar %	Propionate (mg/L) Molar %	Acetate (mg/L) Molar %	Butyrate (mg/L) Molar (%)	Isobutyrate (mg/L) Molar %	Isovalerate (mg/L) Molar %	Valerate (mg/L) Molar %	Hexanoate (mg/L) Molar %
TAN-25	23	1,700	0 [b] 1%	230 17%	540 49%	356 22%	95 6%	86 4%	20 1%	9 [a]0%
TAN-25	37	211	0 0%	0 [a] N/A	10 17%	0 [a] N/A	2 2%	76 74%	0 0%	0 0%
TAN-31	2	12,000	9,800 82%	81 3%	310 15%	0 [a] 0%	0 [a] 0%	0 [a] 0%	0 0%	0 0%
TAN-31	4	7,900	3,500 51%	135 9%	450 38%	3 [a]0%	4 [a]0%	12 1%	0 0%	0 0%
TAN-31	8	4,400	0 [b] 0%	940 34%	1,250 56%	346 10%	0 [a] 0%	0 [a] 0%	0 0%	0 0%
TAN-31	23	612	0 0%	110 23%	133 35%	178 31%	27 5%	31 5%	10 1%	0 0%
TAN-31	37	110	0 0%	8 18%	21 61%	4 8%	2 5%	0 [a] 0%	0 [a] 0%	0 0%
TAN-1859	8	880	0 0%	260 33%	390 63%	32 4%	0 [a] 0%	0 [a] 0%	0 0%	0 0%
TAN-1859	37	31	0 0%	0 [a] 0%	8 61%	0 [a] 0%	0 [a] 0%	0 0%	0 0%	0 0%

a. These values were reported as <0.223, which means that lactate was detected but was below the MDL. These values are therefore reported here as 0 mg/L.

b. Although there are VFAs present, when the molar percentage was calculated the percent of the VFA was so small that 0% was recorded.

c. Value reported as <5 mg/L, which means that the VFA was detected but was below the MDL. These values are therefore reported here as 0 mg/L.

d. Value reported as <100 mg/L, which means lactose was detected but was below the MDL. These values are therefore reported here as 0 mg/L.

Table 3-7. First order lactate degradation rate constants for November 2003 through February 2004.

Well	November 2003 1X 6% (TSF-05)	December 2003 1X 6% (TAN-1859)	January 2004 1X 6% (TSF-05)	February 2004 2X 3% (TAN-1859)
TSF-05A	0.28	N/A	0.28	N/A
TSF-05B	0.38	N/A	0.33	N/A
TAN-25	0.36	N/A	0.30	N/A
TAN-31	0.28	N/A	0.25	N/A

N/A = not available.

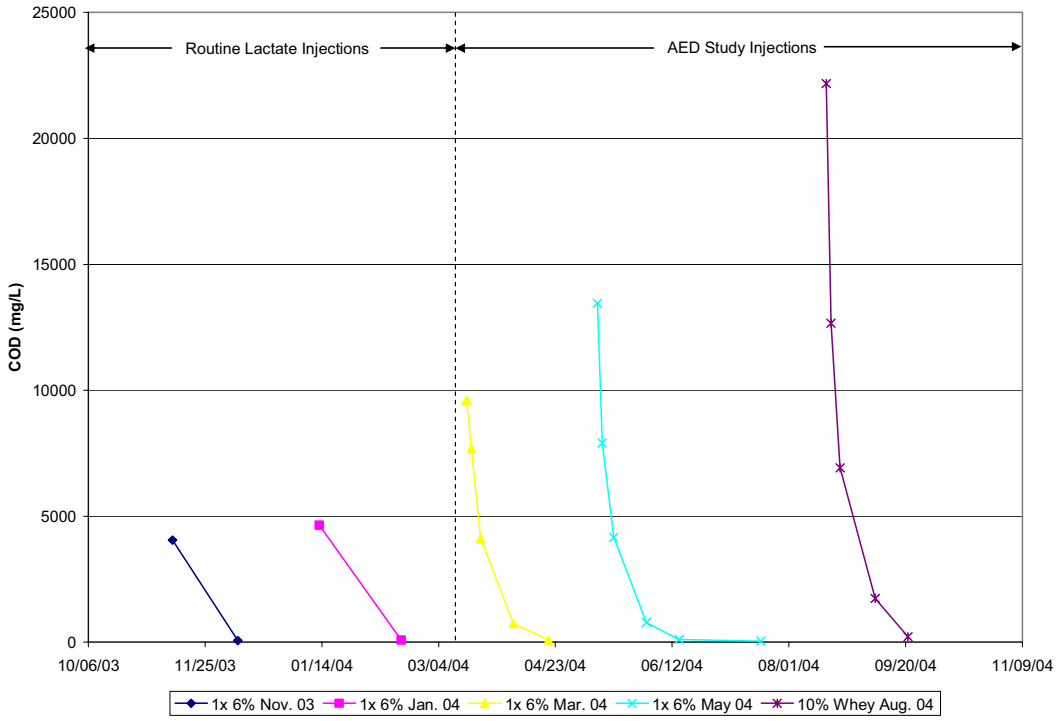

Figure 3-7. Example of chemical oxygen demand drops at TAN-25 following injection events.

The effects of the different injections on electron donor utilization, as indicated by changes in the first order utilization rates of COD and lactate, are presented for biologically active wells TSF-05A, TSF-05B, TAN-25, and TAN-31. Utilization rates could not be calculated for the outside and deep wells because of insufficient distribution of electron donor to these locations. The first order rate law for the consumption of reactant A (electron donor) is:

$$\frac{-d[A]}{dt} = k[A] \tag{3-5}$$

where:

$[A]$ = concentration of A

t = time

k = fraction of A consumed per unit of time (rate constant).

Integration of Equation 3-5 with respect to time leads to:

$$[A]=[A]_0 e^{-kt} \quad (3\text{-}6)$$

where:

$[A]_0$ = initial concentration of A

$[A]$ = concentration of A at time t.

The logarithmic form of Equation 3-6 is:

$$\ln[A]=\ln[A]_0 - kt \quad (3\text{-}7)$$

This implies that the first order rate constant, k, can be determined by plotting ln[A] versus time. The plot is a straight line, with the slope equal to "-k" and the intercept equal to "$\ln[A]_0$". First order rate constants were calculated from the slope of ln[lactate or COD] over time elapsed since each injection using data from TSF-05A, TSF-05B, TAN-25, and TAN-31 (Table 3-7). Table 3-8 presents the estimated first order degradation rate constants for COD after each injection.

Table 3-8. First order chemical oxygen demand degradation rate constants for November 2003 through February 2004.

Well	November 2003 1X 6% (TSF-05)	December 2003 1X 6% (TAN-1859)	January 2004 1X 6% (TSF-05)	February 2004 2X 3% (TAN-1859)
TSF-05A	0.18	N/A	0.15	N/A
TSF-05B	0.16	N/A	0.14	N/A
TAN-25	0.15	N/A	0.12	N/A
TAN-31	0.12	N/A	0.13	N/A

N/A = not available

Lactate degradation rate constants for all of the biologically active wells were similar for each of the 1X 6% injections in TSF-05 for the reporting period, ranging from 0.25 to 0.38. Utilization rates were not calculated at TAN-1859 after the 1X 6% injections into TSF-05 because these injections produced insufficient lactate in TAN-1859. Similarly, injections in TAN-1859 did not increase lactate in the other wells sufficiently to calculate utilization rates.

The rate constants calculated using COD values estimate the degradation rate for the combined electron donor within the system, providing a more general interpretation of electron donor utilization. Utilization constants for the injections from November 2003 through February 2004 ranged from 0.12 to 0.18 throughout the biologically active wells.

3.1.3.2 AED Optimization (March 2004 through September 2004). This section presents the electron donor utilization rate evaluation following the two AED lactate injections and the first AED whey injection conducted as part of the AED optimization. As stated in Section 2.3, the AED optimization for this reporting period consisted of two injections of a 1x 6% sodium lactate and one injection of a 1x 10% whey powder injection into TSF-05. The parameters used for calculating electron donor utilization within the residual source area were COD and lactate for the sodium lactate injections, and COD and lactose for the whey powder injection.

Additional data points were collected during the AED optimization to calculate more rigorous first-order rate constants, the metric used to compare the utilization of the different electron donor solutions. Utilization rates calculated in the FY 2002 Annual Report (INEEL 2003a) were based upon two data points collected between injections (approximately 8–10 and 36–38 days following an injection). Following an AED optimization injection, samples were collected from the biologically active wells at approximately Days 2, 4, 8–10, 22 or 23, and 36–38. First order rate constants were then calculated using methods outlined in Section 3.1.3.1 with these additional data collected following each injection. The COD utilization rate constants were calculated using COD data from the Day 2 through 36–38 sampling events after each AED injection. This corresponds to the total duration of the electron donor as primary and secondary substrates. The primary substrates lactate and lactose, however, were depleted more rapidly than the total COD and so only data collected when the primary substrates were present were used. For lactate, utilization rate constants were calculated using the Day 2 through Day 22 or 23 sampling events. For lactose, utilization rate constants were calculated using only Day 2 through Days 8–10 sampling events.

Table 3-9 presents the first order degradation rate constants for lactate in Wells TSF-05A, TSF-05B, TAN-25, and TAN-31 based on the two baseline lactate injections and the first whey powder injection. Degradation rate constants ranged from 0.27 to 0.48 day^{-1} at all of the AED well locations. TSF-05A and TSF-05B had the highest lactate utilization rate constants following the first lactate injection (0.47–0.48 day^{-1}), followed by TAN-25 and TAN-31 (0.29 day^{-1}). Similar trends in lactate utilization rate constants were calculated following the second lactate injection. TSF-05B had the highest lactate rate constant (0.48 day^{-1}), then TSF-05A (0.44 day^{-1}), followed by TAN-31 (0.36 day^{-1}), and TAN-25 (0.27 day^{-1}). The rates calculated following multiple injections are within 10% for each well, with the exception of TAN-31, indicating good reproducibility. Table 3-10 presents the first order degradation rate constants calculated for COD in Wells TSF-05A, TSF-05B, TAN-25, and TAN-31 based on Days 2 through 36–38 following each sodium lactate and whey injection.

The degradation rate constants calculated for lactate during the AED optimization are reported in Table 3-9. After the two baseline lactate injections, the degradation rate constants ranged from 0.27 to 0.48 day^{-1} at all of the AED well locations. Wells TSF-05A and TSF-05B had the highest lactate utilization rate constants following the first lactate injection (0.47–0.48 day^{-1}), followed by TAN-25 and TAN-31 (0.29 day^{-1}). Similar trends in lactate utilization rate constants were calculated following the second lactate injection. TSF-05B had the highest lactate rate constant (0.48 day^{-1}), then TSF-05A (0.44 day^{-1}), followed by TAN-31 (0.36 day^{-1}), and TAN-25 (0.27 day^{-1}). Comparison of the rates following the two baseline lactate injections showed that the rates were within 10% for each well, with the exception of TAN-31, indicating good reproducibility.

Table 3-9. First order lactate and lactose degradation rate constants for the alternate electron donor optimization.

Well	1st Sodium Lactate Injection (day^{-1}) (Days 2, 4, 8–10, 22 or 23)	2nd Sodium Lactate Injection (day^{-1}) (Days 2, 4, 8–10, 22 or 23)	1st Whey Powder Injection (day^{-1}) (Days 2, 4, 8–10)
TSF-05A	0.48	0.44	0.95
TSF-05B	0.47	0.48	0.48
TAN-25	0.29	0.27	0.97
TAN-31	0.29	0.36	0.91

Table 3-10. First order chemical oxygen demand degradation rate constants for the alternate electron donor optimization.

Well	1st Sodium Lactate Injection (day^{-1})	2nd Sodium Lactate Injection (day^{-1})	1st Whey Powder Injection (day^{-1})
TSF-05A	0.14	0.15	0.15
TSF-05B	0.10	0.11	0.12
TAN-25	0.14	0.13	0.12
TAN-31	0.15	0.17	0.13

After the whey powder injection, the degradation rate constants were calculated for the primary substrate lactose for each of the AED well locations. In general, the utilization rate constants calculated for lactose were much higher than for lactate. For instance, Well TSF-05A had a lactate utilization rate constant of approximately 0.46 day^{-1} and a lactose utilization rate constant of 0.95 day^{-1}. Likewise, TAN-25 was approximately 0.28 day^{-1} for lactate and 0.97 day^{-1} for lactose, and TAN-31 was 0.33 day^{-1} for lactate and 0.91 day^{-1} for lactose. In contrast, the utilization rate constants calculated for lactate and lactose were approximately the same at TSF-05B (0.47–0.48 day^{-1}) following sodium lactate and whey powder injections.

The rate constants calculated using COD values represent a measure of the degradation rate for the combined electron donor within the system, providing a more general interpretation of electron donor utilization. The estimated rates are lower than the rates calculated for the primary substrates lactate and lactose because they inherently include the production and subsequent degradation of the secondary substrates (e.g., propionate and acetate), which are degraded at much slower rates than the primary substrates. The rate constants calculated using COD data for TSF-05A, TSF-05B, TAN-25 and TAN-31 ranged from 0.10 to 0.15 day^{-1} following the March 2004 sodium lactate injection and from 0.11 to 0.17 day^{-1} following the May 2004 sodium lactate injection (see Table 3-8). After both injections, TSF-05B had the lowest utilization rate constant and TAN-31 had the highest.

3.2 Redox Conditions

In order for ARD of chloroethenes to proceed to completion at meaningful rates, the process must be energetically favorable. Therefore, the complete transformation of TCE to ethene by ARD requires the absence of competing electron acceptors like oxygen, nitrate, ferric iron, manganese (IV), and sulfate. The ARD of TCE to cis-DCE requires redox conditions in the range of iron and sulfate reduction, but complete dechlorination to ethene requires redox conditions that support methane production. At TAN, the most efficient ARD observed has been correlated to the onset of significant methanogenesis. Methanogenic conditions are indicated by the absence of sulfate (and other electron acceptors), the presence of ferrous iron, and the presence of methane. The locations that have achieved methanogenic redox conditions at TAN are those to which significant quantities of electron donor have been distributed. Redox charts for all wells are presented in Appendix C.

3.2.1 Biologically Active Wells - TSF-05 Injections (November 2003 and January 2004)

Wells in the vicinity of TSF-05 (TSF-05A, TSF-05B, TAN-25, TAN-31, and TAN-1859) remained methanogenic throughout this period of lactate injections into TSF-05. This is demonstrated by the complete reduction of sulfate, elevated ferrous iron concentrations, and significant methane production, as evidenced by methane concentrations approaching solubility in the source area. Decreases in methane concentrations immediately following injection events are likely the result of dilution by the injected fluid.

3.2.2 Biologically Active Wells - TAN-1859 Injections (December 2003 and February 2004)

Ferrous iron concentrations at TAN-1859 increased substantially following injections at this location, with concentrations increasing to over 3.00 mg/L, up from pre-injection concentrations of approximately 0.50 to 0.75 mg/L. Sulfate concentration remained at 0 mg/L throughout the routine lactate injections. Methane at this location remained fairly consistent, with concentrations ranging from 10,000 to 15,000 µg/L.

3.2.3 Biologically Active Wells - AED Optimization Sodium Lactate Injections in Well TSF-05 (March 2004 and May 2004)

Following the AED optimization sodium lactate injections, ferrous iron concentrations generally remained between 3 to 6 mg/L. Sulfate concentrations remained 0 mg/L for all sampling points except the July 19, 2004 sampling event at TSF-05A (23 mg/L), which corresponded to 71–73 days following the second lactate injection. Methane concentration initially dropped at all AED well injections (likely as a result of dilution due to the injection solution) and then rebounded, suggesting active methanogenesis.

3.2.4 Biologically Active Wells - AED Optimization Whey Injection in Well TSF-05 (August 2004)

Redox parameters also were affected following the whey powder injection. The ferrous iron concentration generally remained between 4 to 5 mg/L. Sulfate concentration spikes (~14 mg/L) were observed at all of the AED well locations on Days 2 and 4 following the whey injection but declined to 0 mg/L by the Day 22 or 23 sampling event. Methane concentration dropped following whey powder injection (on Days 2 and 4) but increased dramatically thereafter (Days 8–10 to 36–38).

3.2.5 Outside and Deep Wells - All Injections

Methane concentrations at TAN-37A ranged from approximately 8,000 to 17,000 µg/L during injections and concentrations at TAN-37B were somewhat higher, ranging from 11,000 to 18,000 µg/L. These high methane concentrations are likely the result of methane flux from the biologically active area. Sulfate concentrations at both locations have remained steady at approximately 35 to 40 mg/L. The nominal concentrations of sulfate and low concentrations of ferrous iron at outside locations indicate that these locations are anaerobic but not methanogenic.

The deep locations (TAN-26 and TAN-37C) remain methanogenic, as evidenced by high concentrations of methane, elevated ferrous iron concentrations, and complete sulfate reduction. Overall, methane concentrations remain high at the crossgradient and downgradient locations, with concentrations over 3,000 µg/L. Sulfate in the outside wells remains steady with concentrations throughout the area remaining at approximately 40 mg/L. Well TAN-D2 is the only well of the outside well cluster impacted by lactate injections in TSF-05. Well TAN-D2 was methanogenic to near-methanogenic, as evidenced by sporadic sulfate reduction, high methane concentrations, and elevated ferrous iron concentrations.

3.3 Anaerobic Reductive Dechlorination

During this reporting period, the efficiency of the ARD reactions was assessed by examining changes in relative concentrations of trichloroethene (TCE), cis-1,2-dichloroethene (cis-DCE), vinyl chloride (VC), and ethene. High concentrations of ethene relative to TCE, cis-DCE, and VC indicate that ARD reactions are operating efficiently.

3.3.1 Biologically Active Wells - TSF-05 Injections (November 2003 and January 2004)

The ARD has continued in all biologically active wells throughout the reporting period. Ethene represents the highest mole fraction at TSF-05A and TSF-05B (Figures 3-8 and 3-9). After injections in TSF-05, molar concentrations of TCE increased in the days following the injection and subsequently decreased over time, while the mole fraction of ethene increased with time after injection, as TCE that was liberated during each injection was dechlorinated. Ethene concentrations were highest at TSF-05, with concentrations typically ranging from 100 to 300 µg/L. This general trend also is observed at TAN-25 and TAN-31, with TCE and/or cis-DCE concentration spikes after the injection followed by conversion to ethene. Overall, total VOC and ethene concentrations at TAN-25 and TAN-31 are lower than those at TSF-05.

Trans-DCE continued to be a relatively recalcitrant compound at each of the biologically active wells, representing the highest mole fraction at TAN-25 and TAN-31, although concentrations appear to be declining from approximately 200 µg/L in these wells at the beginning of the reporting period to 150 µg/L at the end of the period (Figures 3-10 and 3-11). Similar trends were observed at TSF-05. At TSF-05A and TSF 05B, the predominant compound is ethene, while at Wells TAN 25 and TAN 31, the dominant compound is trans-DCE.

3.3.2 Biologically Active Wells - TAN-1859 Injections (December 2003 and February 2004)

TAN-1859 was the only monitoring location that responded to the injections in this location. All VOC concentrations at TAN-1859 remained stable, with TCE remaining below the detection limit and concentrations of cis-DCE, trans-DCE, and VC remaining relatively stable. None of the other wells in the biologically active zone showed any impacts directly from injections in TAN-1859.

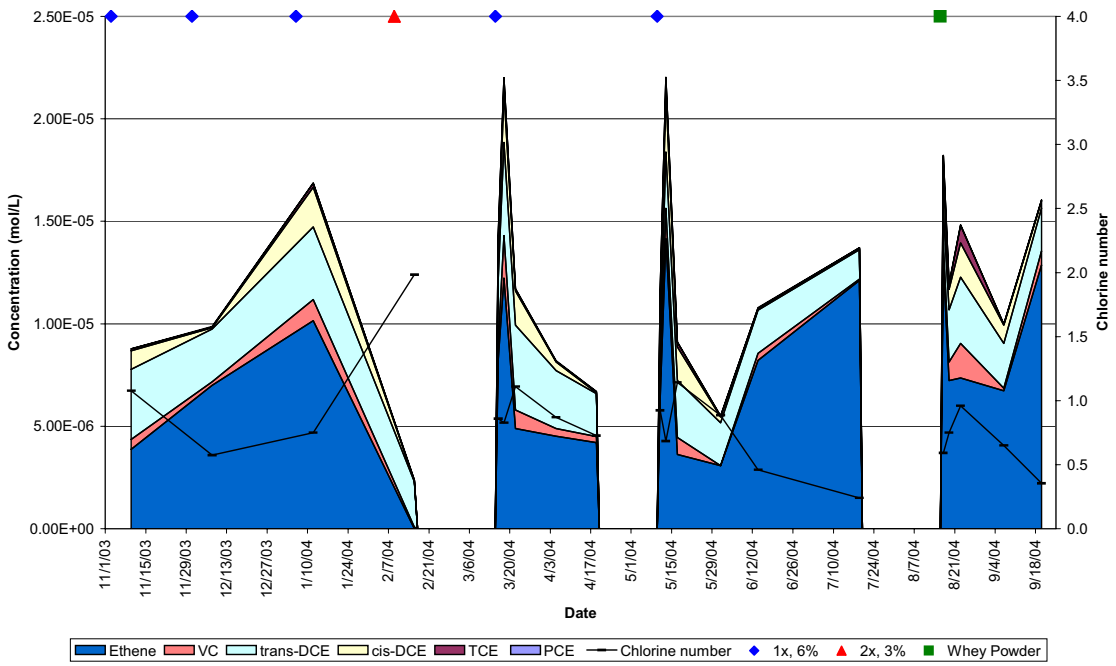

Figure 3-8. Anaerobic reductive dechlorination at Well TSF-05A.

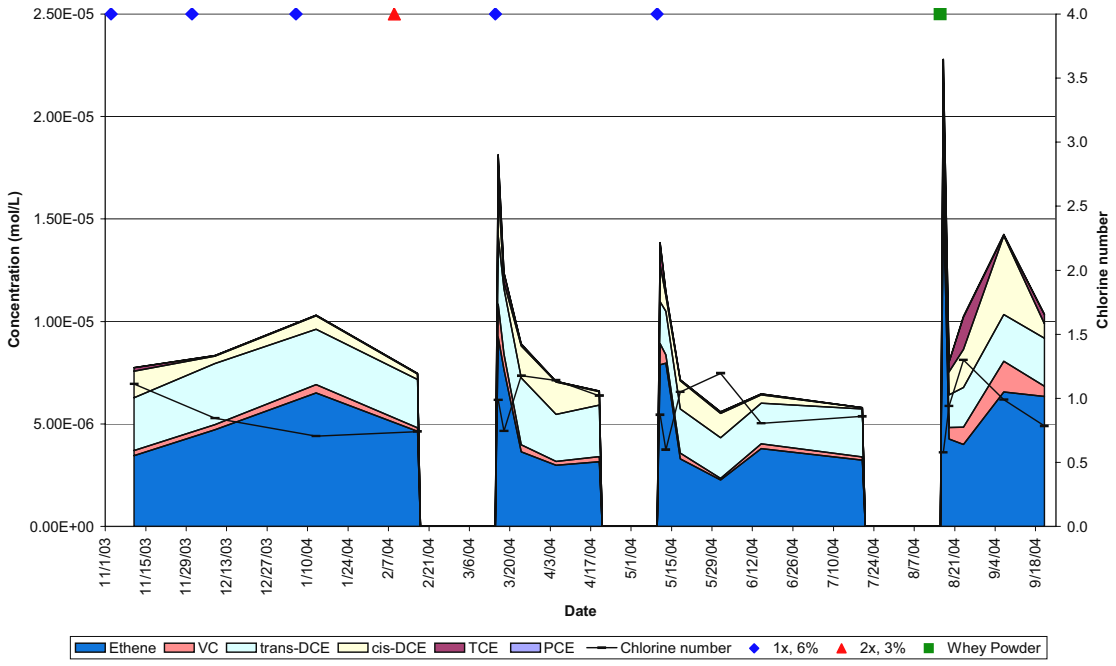

Figure 3-9. Anaerobic reductive dechlorination at Well TSF-05B.

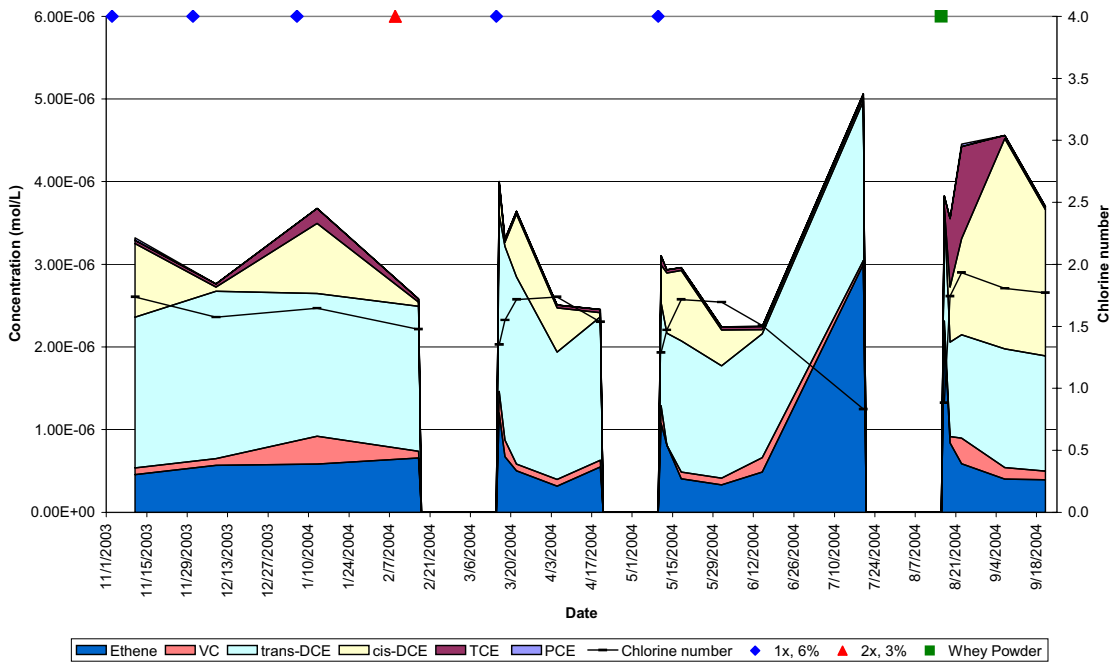

Figure 3-10. Anaerobic reductive dechlorination at TAN-25.

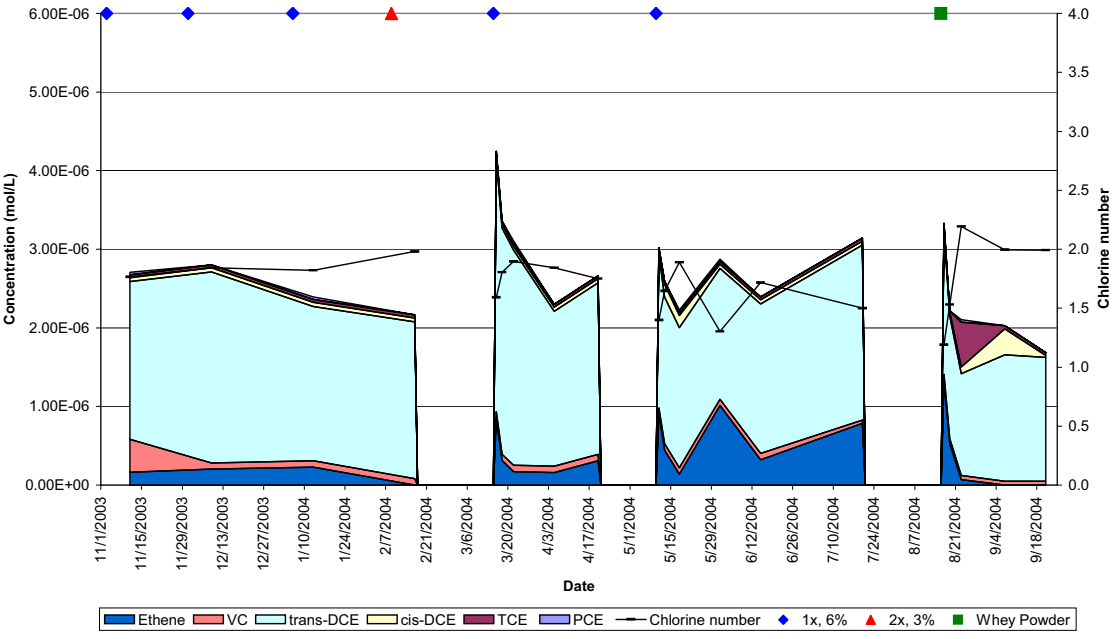

Figure 3-11. Anaerobic reductive dechlorination at Well TAN-31.

3.3.3 Biologically Active Wells - AED Optimization Sodium Lactate Injections in Well TSF-05 (March 2004 and May 2004)

The samples collected at Days 2 and 4 following an injection provided a higher-resolution picture of the residual source response to the sodium lactate injections. At TSF-05A, VOC and ethene concentrations were near 0 µg/L prior to the March 2004 sodium lactate injection, but increased dramatically on Day 2 following the injection, with TCE reaching its peak concentration of 120 µg/L. Concentrations of the other VOCs peaked on Day 4 with cis-DCE at 241 µg/L, 129 µg/L for VC, and 343 µg/L for ethene. By Days 8–10, concentrations had decreased to 11 µg/L for TCE, 160 µg/L for cis-DCE, 57 µg/L for VC, and 137 µg/L for ethene. Concentrations were nearly depleted by the Days 36–38 sampling event, with only VC above MCLs (18 µg/L) and ethene present at 118 µg/L. This trend was replicated nearly perfectly at TSF-05A after the May sodium lactate injection. At TSF-05B (Figure 3-9), baseline ethene concentrations were approximately 100 µg/L before and after the sodium lactate injections. Following the March 2004 sodium lactate injection, high concentrations of VOCs (TCE at 62 µg/L, cis-DCE at 228 µg/L, VC at 101 µg/L, and ethene at 259 µg/L) were observed on the Day 2 sampling event. However, less efficient reductive dechlorination was observed at TSF-05B as compared to TSF-05A, which was demonstrated by persistent cis-DCE concentrations at approximately 150 µg/L until the May 2004 sodium lactate injection.

Following the May 2004 sodium lactate injection, VOC concentrations again spiked at TSF-05B, reaching peak concentrations on Day 2 of 140 mg/L for TCE, 174 mg/L for cis-DCE, 64 mg/L for VC, and 222 mg/L for ethene. By the Days 71–73 sampling event (July 19, 2004), no chlorinated ethenes were observed at either TSF-05 well locations, with only ethene present. The relative mass of ethene, however, was dramatically higher at TSF-05A (340 mg/L) at the Days 71–73 sampling event than at the Days 36–38 sampling event (231 mg/L). Ethene concentrations at TSF-05B on the Days 71–73 sampling event, however, were slightly lower than the Days 36–38 sampling event (91 vs. 106 mg/L).

Total chlorinated ethene concentrations at Wells TAN-25 and TAN-31 also increased following the two lactate injections, although the magnitude of the spikes was much lower than in TSF-05A and TSF-05B. The VOC concentration spikes following the March 2004 sodium lactate injection at TAN-25 were: cis-DCE at 35 µg/L, VC at 17 µg/L, and ethene at 34 µg/L (TCE was not detected). By the Days 36–38 sampling event, the chlorinated ethene concentrations had declined to near 0 µg/L. The same trend was observed following the May 2004 sodium lactate injection, with concentrations increasing to 15 µg/L for TCE, 44 µg/L for cis-DCE, 13 µg/L for VC, and 30 µg/L for ethene. By the Days 71–73 sampling event, all VOCs were depleted at TAN-25 and ethene concentrations had dramatically increased to 84 µg/L. The VOC response to sodium lactate injections at TAN-31 was observed primarily as spikes in ethene concentrations. Following the first sodium lactate injection, ethene increased from 0 to 24 µg/L by the Day 2 sampling event. Following the second lactate injection, ethene increased from 0 to 25 µg/L and cis-DCE increased from 0 to 16 µg/L.

Figures 3-8 through 3-11 illustrate the VOC molar response to electron donor injections in the AED sample locations. Total VOC and ethene concentrations increased by a factor of 103 and 66 at TSF-05A, 2.89 and 2.87 at TSF-05B, 2.26 to 2.58 at TAN-25, and 6.04 and 2.23 at TAN-31 following the March and May 2004 sodium lactate injections compared to concentrations observed prior to injection. These factors were calculated relative to the last sampling event prior to the particular injection. The TSF-05A values are significantly higher than other AED locations because total VOC and ethene concentrations were near zero prior to the injection events. These concentration increases were clearly correlated to the injections, as concentrations returned approximately to pre-injection concentrations 22 or 23 days following the injection. However, ethene concentrations at the Days 71–73 sampling event following the May 2004 sodium lactate injection increased dramatically at TSF-05A with total VOC and

ethene concentrations increasing by a factor of 3.60 over concentrations observed at the Days 22 sampling event. Likewise, total VOC and ethene concentrations increased by a factor of 3.57 at TAN-25.

3.3.4 Biologically Active Wells - AED Optimization Whey Injection in Well TSF-05 (August 2004)

The whey powder injection into TSF-05 also resulted in increased concentrations of total VOCs and ethene following the August 2004 injection (see Appendix C). The enhanced dissolution effects can be seen by spikes in TCE, cis-DCE, VC, and ethene concentrations observed at Days 2 and 4 in TSF-05A (131 µg/L for TCE, 159 µg/L for cis-DCE, 65 µg/L for VC, and 362 µg/L for ethene) and TSF-05B (152 µg/L for TCE, 206 µg/L for cis-DCE, 94 µg/L for VC, and 453 µg/L for ethene), as compared with ethene concentrations of 340 µg/L in TSF-05A and 91 µg/L in TSF-05B prior to whey injection. Efficient reductive dechlorination of these newly liberated contaminants was evidenced by accumulation of reductive daughter products cis-DCE, VC and finally ethene. By Days 36–38 following the whey injection, ethene concentrations predominated for TSF-05A (361 µg/L) compared to cis-DCE (34 µg/L) and VC (43 µg/L), and for TSF-05B (178 µg/L) compared to TCE (58 µg/L), cis-DCE (68 µg/L), and VC (31 µg/L).

The peak VOC and ethene concentrations were observed at Days 4 and 7 for TAN-25 and TAN-31 following the whey powder injection. At TAN-25, TCE concentrations increased from 0 µg/L prior to the whey powder injection to 147 µg/L at the Day 7 sampling event. Likewise, cis-DCE concentrations increased from 0 µg/L prior to whey injections to a peak concentration of 247 µg/L on Day 22. At TAN-31, a TCE concentration spike (75 µg/L) also was observed on the Day 7 sampling event followed by a spike in cis-DCE (32 µg/L) on the Day 22 sampling event following whey powder injection. Ethene concentrations at TAN-25 declined following the whey injection, as compared to the prior Day 71 sampling event (62 vs. 84 µg/L), and declined further to approximately 10 µg/L by the Day 7 and 22 sampling events. A similar trend was observed at TAN-31, with ethene concentrations declining from 37 µg/L on the Day 2 sampling event to 0 µg/L on the Day 22 sampling event.

3.3.5 Outside and Deep Wells - All Injections

Concentrations of TCE at TAN-37A decreased from 202 µg/L on December 8, 2003 to 67 µg/L on May 17, 2004. Concentrations of TCE at TAN-37B dropped from 146 µg/L on December 8, 2003 to 56 µg/L on May 17, 2004 (Figure 3-12). During this timeframe, trans-DCE concentrations showed slight increases from 151 µg/L to 164 µg/L with a peak of 214 µg/L, and cis-DCE also increased from 14 µg/L to 23 µg/L, with a peak of 37 µg/L. Vinyl chloride fluctuated between a low of 14 µg/L and high of 36 µg/L. Similar trends to these TAN-37B trends also were observed at TAN-37A.

Chlorinated ethene concentrations at TAN-26, with the exception of trans-DCE, have been near or below MCLs since January 2000. Trans-DCE concentrations (MCLs of 100 µg/L) were between 80 to 130 µg/L at this well. For Well TAN-37C, TCE and cis-DCE were below MCLs (5 and 70 µg/L, respectively) during this reporting period. In general, VC also was below the MCL of 2 µg/L, with the exception of the February 16, 2004 concentration of 24.6 µg/L. Trans-DCE remained near or below the MCL of 100 µg/L at this location from November 2003 through February 2004 but subsequently increased in concentrations (100 to 125 µg/L) during the later part of the reporting period (March 2004 through September 2004).

Chlorinated ethene concentrations in outside wells have shown little change during this reporting period compared with previous reporting periods. TCE concentrations for outside and deep wells collected during this reporting period are shown in Figure 3-12. Significant ARD has not been observed at

TAN-37A or TAN-37B, with TCE concentrations ranging from approximately 75 to 150 µg/L at TAN-37A and 50 to 150 µg/L at TAN-37B. All VOCs at TAN-10A were near or below MCLs during the entire reporting period. The TCE concentrations at TAN-27 were generally steady, with values at approximately 40 µg/L. Sporadic detections of tetrachloroethene (PCE) have been observed at this location; however, these appeared to be isolated spikes rather than representative of an overall increasing trend. All other VOCs at TAN-27 were nondetect for all samples collected during the reporting period. The VOC concentrations at TAN-29 remained fairly constant throughout the reporting period and are similar to concentrations observed since January 2002. The TCE concentrations at TAN-28 ranged from 800 to 1,000 µg/L, which is similar to concentrations observed throughout the duration of ISB operations. The other VOC concentrations remained steady throughout the reporting period. TCE concentrations at TAN-1860 remained steady at approximately 100 µg/L throughout routine lactate injections; however, concentrations increased sharply starting in April 2004, peaking at 438 µg/L on July 16, 2004. The TCE concentrations have since declined somewhat to approximately 300 µg/L. TCE concentrations at TAN-861 are steady at approximately 100 µg/L.

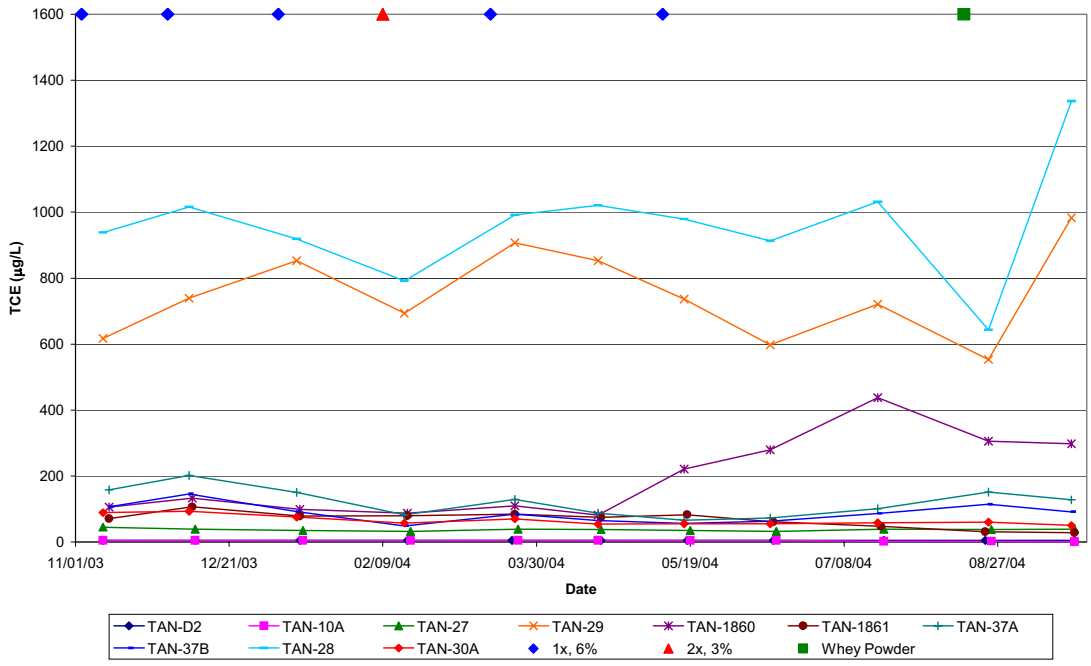

Figure 3-12. Trichloroethene concentrations at the outside and deep wells.

3.4 Biological Activity Indicators

Changes in alkalinity concentrations are an indicator of biological activity in the ISB treatment area. Increases in alkalinity, in this instance, are indicative of the production of carbon dioxide as bicarbonate during fermentative and oxidative reactions. Alkalinity continues to be high throughout the system, with concentrations ranging from 1,000 to 6,000 mg/L in the biologically active wells and deep wells and 200 to 600 mg/L in the outside locations. Alkalinity charts for all wells are shown in Appendix C. Following the injection of whey powder, all of the AED wells showed a pH drop from an initial range of 6.3 to 6.7 to approximately 5.5 by Days 4 through 8–10; however, the pH rebounded to near pre-injection levels by Day 22 or 23.

3.5 Radiological Monitoring

Previous ISB Annual Reports (INEEL 2002a; INEEL 2003a; Armstrong et al. 2004) concluded that although radionuclides were being mobilized in the vicinity of TSF-05 in response to amendment injections, concentrations were being rapidly attenuated so that areas downgradient of the ISB treatment cell were not substantially affected. For part of the AED optimization, Sr-90 monitoring frequency was increased to monthly for the AED wells. Tritium was monitored at all well locations on a monthly basis since tritium data can be indicative of changes in source release rates or other hydrogeologic changes.

The high-frequency collection of Sr-90 during this reporting period show peak concentrations immediately following injections; however, these peak concentrations are within the same ranges as concentrations reported throughout ISB operations at TSF-05A, TSF-05B, TAN-25, and TAN-31. Sr-90 data for TAN-25 is shown in Figure 3-13 as an example. Tritium concentrations do not appear to correlate with injections and remained relatively stable throughout the reporting period for all biologically active wells. Tritium concentrations at TAN-25 for the reporting period are shown in Figure 3-14 as an example.

3.6 Water Quality Monitoring

During this reporting period, multiparameter water quality instruments were used to collect water quality from a subset of ISB wells. Details about instruments, deployment locations, and timeframes of deployment are stated in Section 2.4. During this reporting period, multiparameter water quality instruments were deployed in the biologically active wells TAN-25 and TAN-31 and in the downgradient wells TAN-37 (A and B depths), TAN-28, TAN-30A, TAN-1860, and TAN-1861. In addition, a multiparameter water quality instrument was deployed in TAN-1859 during sodium lactate injections into TSF-05 or in TSF-05 during sodium lactate injections into TAN-1859. Water quality instrument maintenance logs are located in Appendix B and all data are reported in Appendix C.

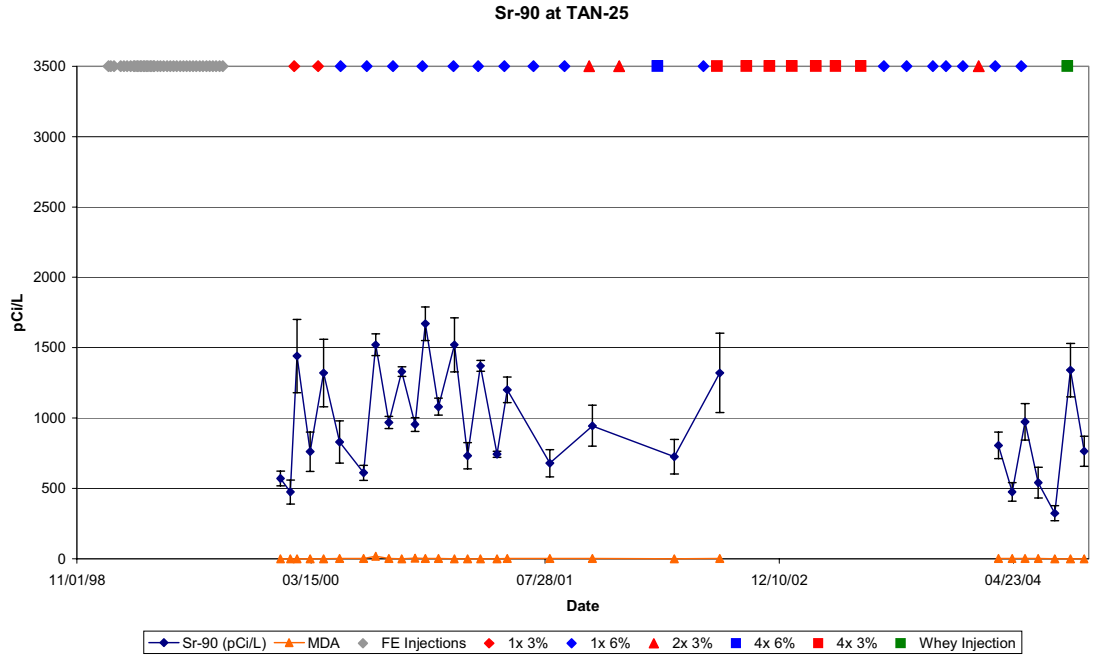

Figure 3-13. Strontium-90 concentrations at Well TAN-25.

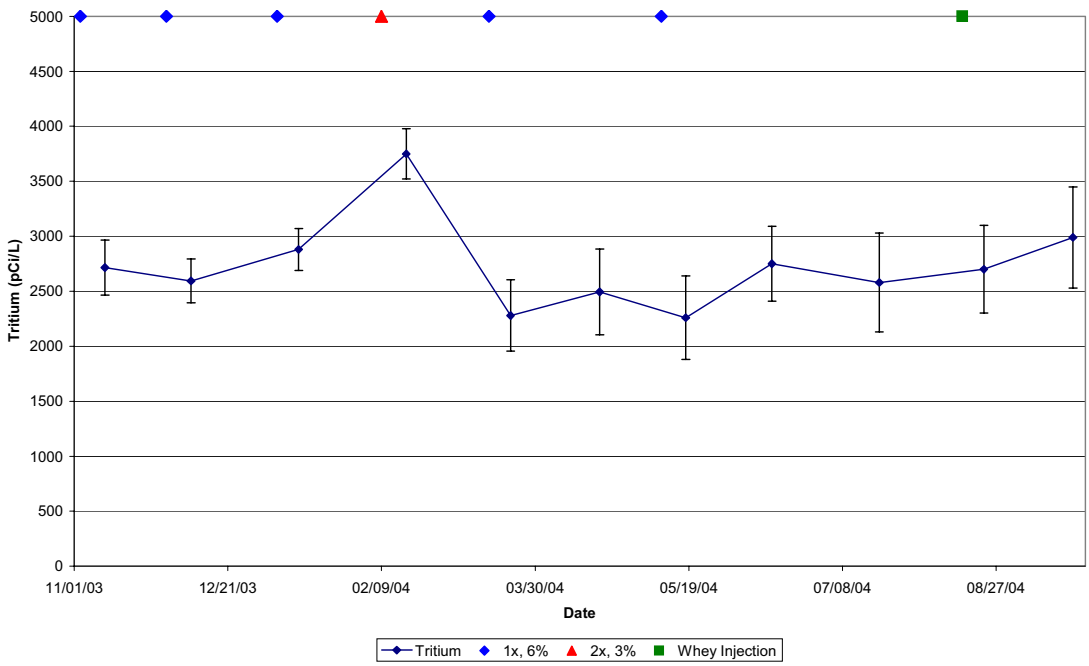

Figure 3-14. Tritium concentrations at Well TAN-25.

In the biologically active wells, spikes in specific conductance showed the distribution of sodium lactate following each injection. Following each spike, specific conductance values gradually decreased until the next electron donor injection. Temperature and ORP data also were used to assess the aquifer conditions for ARD in the source area. Figure 3-15 illustrates that at TAN-31 conductivity increased by approximately 20 to 25 mS/cm in response to injections into TSF-05. In addition, ORP increased at TAN-31 during all injections into TSF-05, but showed a decrease during the December 1, 2003 injection into TAN-1859. Between injections, ORP gradually returned to a level of approximately –430 mV.

Figure 3-16 illustrates that conductivity in TAN-1859 increased by approximately 6 to 7 mS/cm in response to injections into TSF-05 while ORP decreased during the November 2003 injection. ORP values appeared to have stabilized prior to the injection into TSF-05 in January 2004, and only showed a slight decrease in response to this injection. During sodium lactate injections into TAN-1859, no changes in specific conductivity or ORP were observed in TSF-05 or TAN-31.

Changes in specific conductivity, ORP, water level, and temperature, in response to sodium lactate injection activities also were monitored at downgradient monitoring locations. All data for these locations are reported in Appendix C. The ORP data collected from TAN-37A ranged from approximately 0 to -450 mV. Figure 3-17 illustrates that ORP data collected from TAN-37B showed reducing conditions, with values ranging from approximately –450 to -485 mV and conductivity spikes were observed at TAN-37B following injections; these spikes were likely the result of flux of higher conductivity water from the residual source area during sodium lactate injections into TSF-05 and the 1X 6% injection into TAN-1859 on December 1, 2003. The conductivity spike during the 2X 3% injection into TAN-1859 on February 9, 2004, was approximately 0.2 mS/cm higher than all of the other injections (conductivity peaked at 1.86 mS/cm). Conductivity at TAN-37A increased slightly (from approximately 0.95 mS/cm to 1.1 mS/cm) after electron donor injections into TAN-1859. These increases are likely the result of the flux of higher conductivity water from the source area during the TAN-1859 injections.

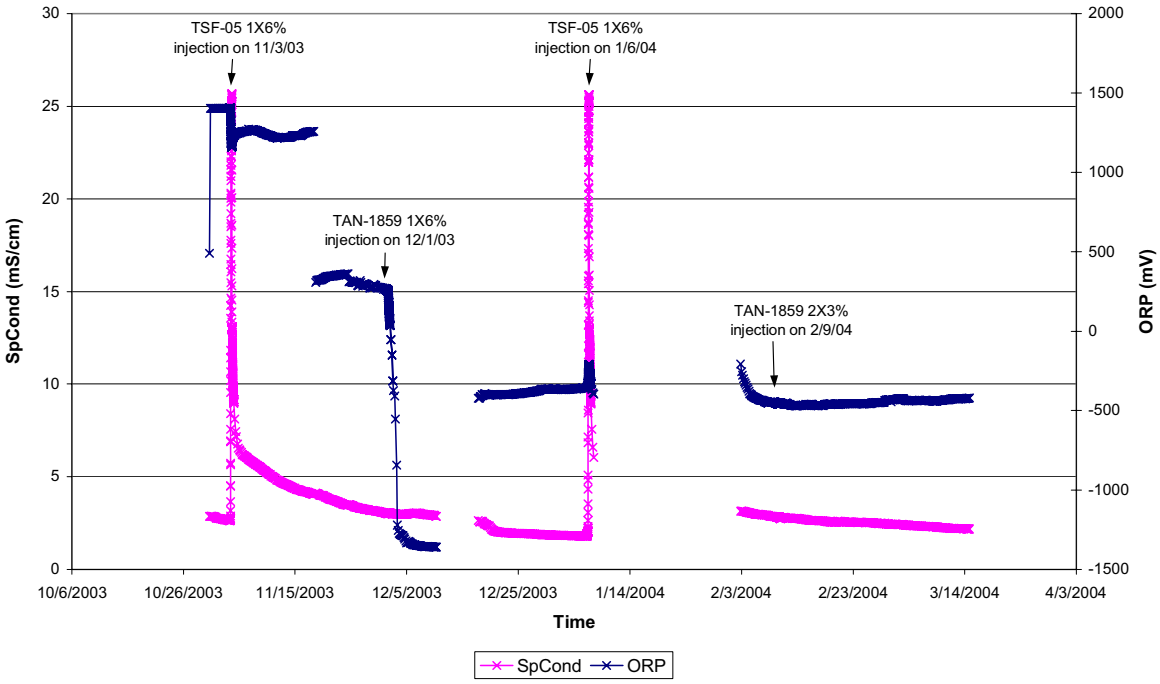

Figure 3-15. Conductivity and oxidation reduction potential at Well TAN-31.

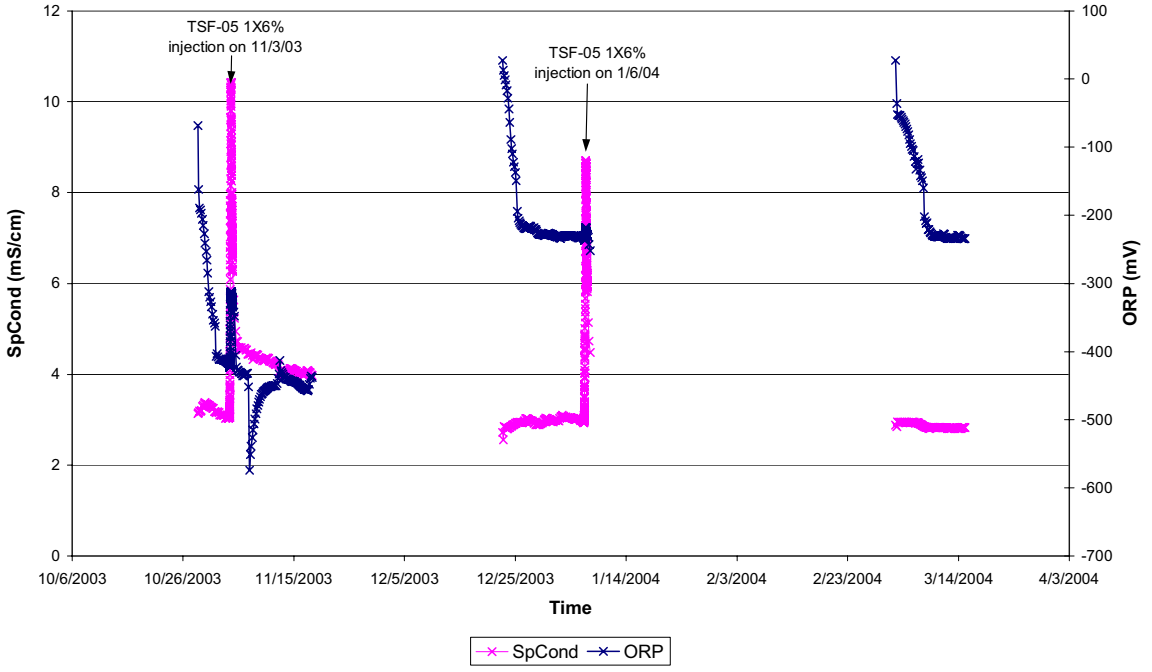

Figure 3-16. Conductivity and oxidation reduction potential at Well TAN-1859.

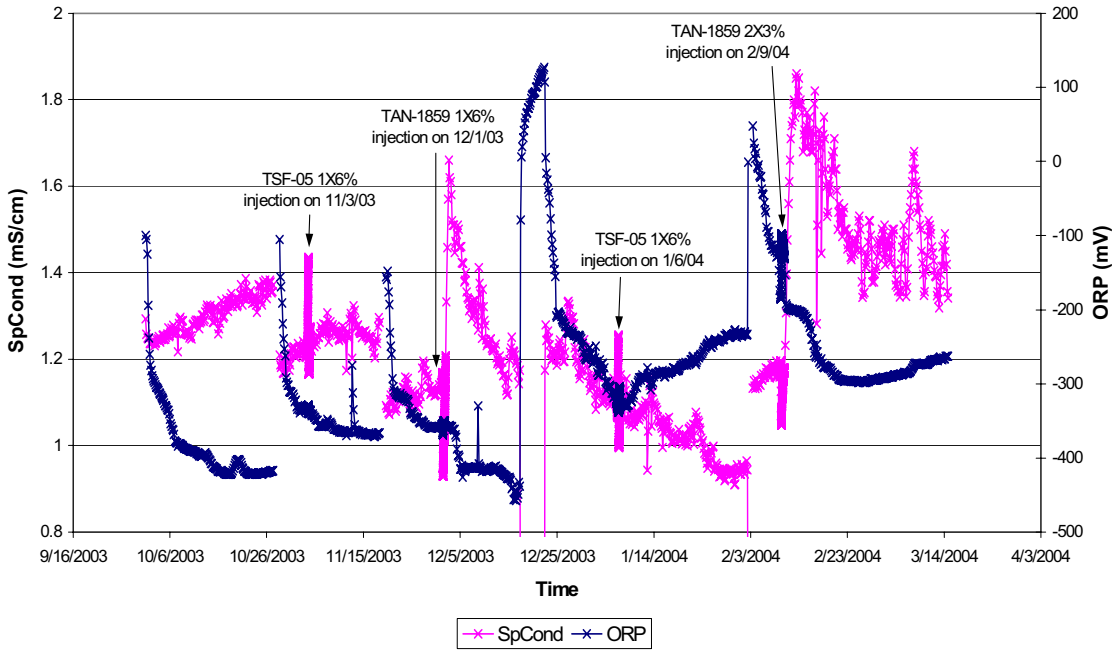

Figure 3-17. Conductivity and oxidation reduction potential at Well TAN-1859.

The other downgradient monitoring locations showed an increase in conductivity immediately following electron donor injections. Similar to the biologically active wells, conductivity gradually decreased following each injection. Increases in conductivity also are likely a result of a flux of higher conductivity water during the injections. These same downgradient monitoring locations showed no change in ORP or temperature that correlated to electron donor injections. These trends are illustrated in Figure 3-18 using TAN-28 data. The data collected from TAN-28 suggest ORP values were usually between approximately 75 to 100 mV, conductivity was between approximately 0.88 to 0.99 mS/cm, and temperature averaged 12.7ºC. Data collected from TAN-30A show ORP values between approximately -333 and –400 mV, conductivity between approximately 1.01 to 1.16 mS/cm, and a temperature average of 12.9ºC. Specific conductivity data collected at TAN-1860 show values ranging widely from approximately 1 to 3 mS/cm. However, following the last calibration event for this multiparameter water quality instrument, values remained steady around 1 mS/cm. This indicated that conductivity values at this monitoring location are most likely approximately 1 mS/cm. The ORP values at this location fluctuated but values usually fell between 75 and –100 mV. In addition, temperature at TAN-1860 averaged 12.9ºC. Data collected from TAN-1861 show that ORP values would periodically spike to approximately –150 mV but values were usually approximately –425 mV. Conductivity at this location ranged between 1.05 to 1.29 mS/cm and the average temperature was 11.4ºC.

The injection strategy for the AED optimization during this reporting period (further described in Section 2.3.1) consisted of two sodium lactate injections and one whey powder injection. Multiparameter water quality instruments were deployed at the same locations as discussed above for the routine lactate injections. Following the first whey powder injection, specific conductivity at TAN-31 and TAN-1859 increased and then gradually decreased, similar to the sodium lactate injections. However, these spikes in conductivity were not as large as the ones following the sodium lactate injections (8.3 mS/cm for TAN-31 and 6.0 mS/cm for TAN-1859), which is consistent with the fact that whey powder is not as ionic as the sodium lactate. The multiparameter water quality instruments at the other locations all showed similar results to the sodium lactate injections (into TSF-05) during the whey injection. This is likely due to the movement of higher conductivity water being moved during the injection.

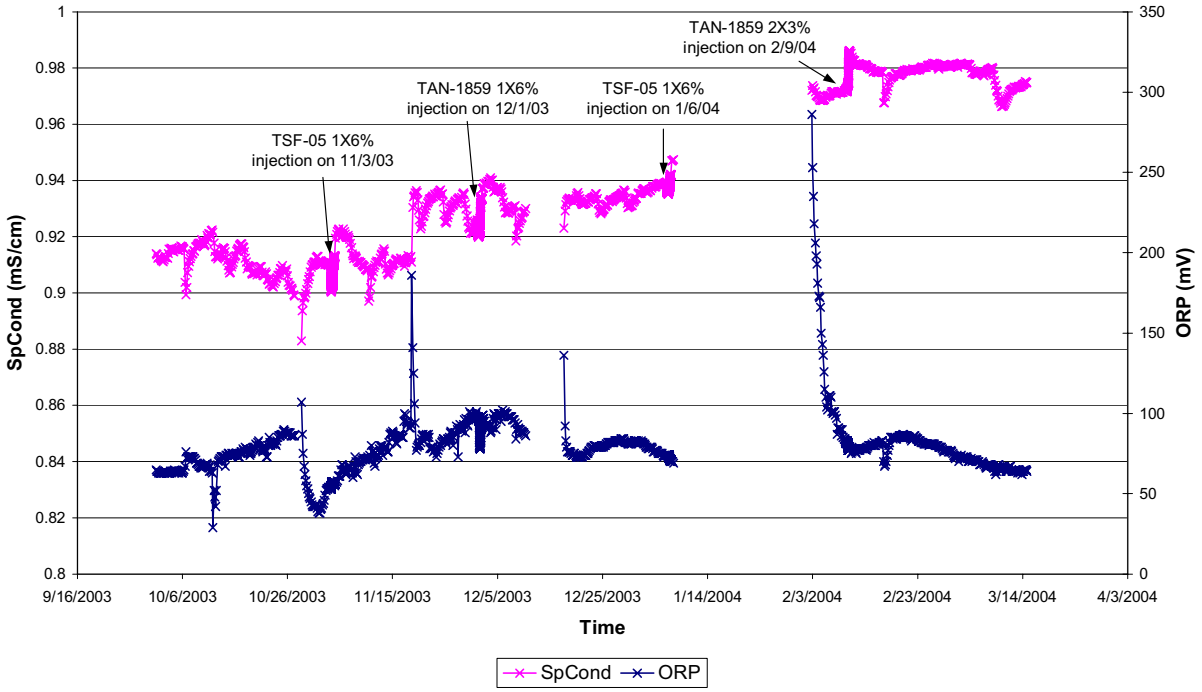

Figure 3-18. Conductivity and oxidation reduction potential at Well TAN-28.

3.7 Water Level Monitoring

Peak observed water level mounding at TSF-05, TAN-25, TAN-31, and TAN-1859 for each electron donor injection during this reporting period is shown in Figure 3-19. Peaks were determined using data collected every 5 minutes from 6:00 AM through midnight on the day of injection. This figure also shows injection dates, volumes and rates, injection location, and electron donor type, which all affect the mounding response. Mounding in Well TSF-05 in early 1999 was approximately 2.5 ft and had increased to approximately 6 ft in 2000. For sodium lactate injections into TSF-05 during this reporting period, mounding in TSF-05 has remained approximately 5 to 6 ft. Less mounding (approximately 0.8 ft) was observed during the sodium lactate injections into TAN-1859 (Figure 3-19, b and d). Also, mounding following the first whey injection into TSF-05 (Figure 3-19, g) showed approximately 5 ft of mounding. Overall, peak mounding for all the wells appears to be consistent throughout this reporting period, which is likely a result of the similar flowrates and volumes used for all electron donor injections. The consistency of these data suggests that biomass was not increasing in the biologically active zone such that flow paths were being affected beyond changes that have already taken place. The relative difference in peak mounding between TAN-25 and TAN-31 did not change during this reporting period, indicating that effective porosity along the flow paths between TSF-05 and TAN-25 and TAN-31 has remained constant.

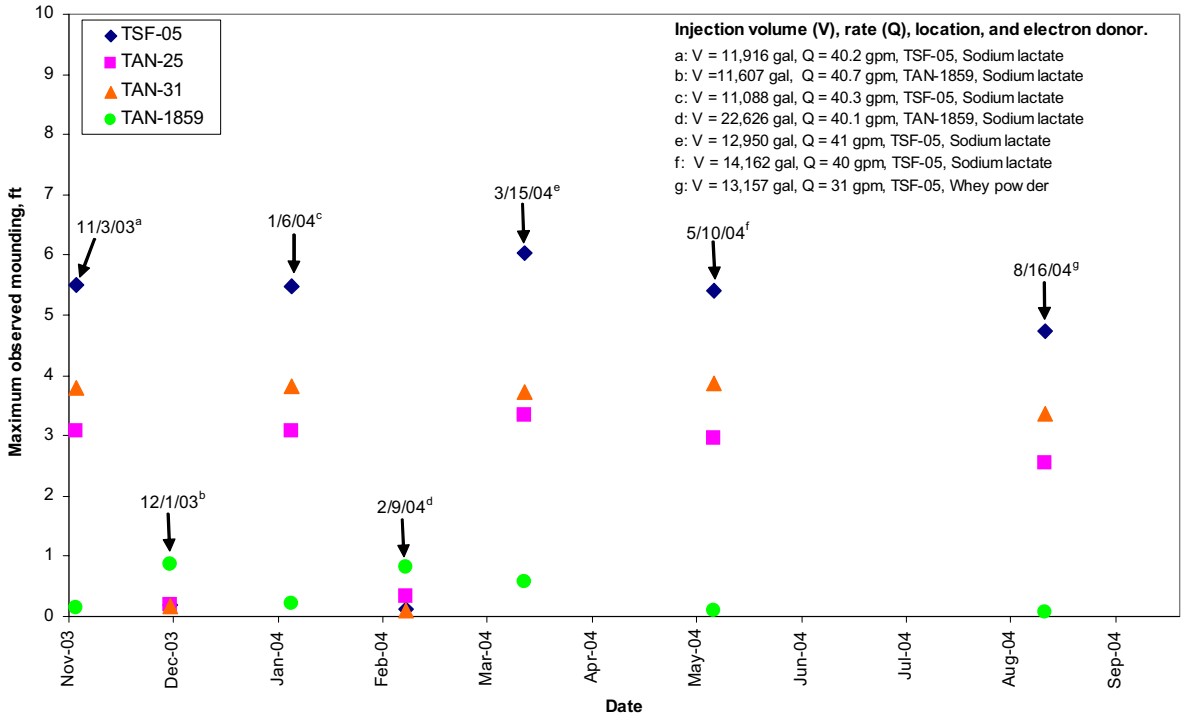

Figure 3-19. Peak water level mounding for electron donor injections during the reporting period.

3.8 Quality Assurance Data

Samples were collected and analyzed during this reporting period in support of quality assurance (QA) requirements for routine sodium lactate injections and the AED optimization. The ISB Groundwater Monitoring Plan (INEEL 2003b) required screening level data with semi-annual definitive confirmation for VOCs, definitive level data for radionuclides, and screening level data for all other analytes. The QA results from this reporting period indicate that the majority of the monitoring data met the applicable quality requirements. Appendix D presents the QA data and summarizes accuracy, precision, and completeness details. Three distinct sets of QA requirements are specified in the Groundwater Monitoring Plan for the three categories of analysis: (1) field laboratory analyses, (2) IRC laboratory analyses, and (3) off-Site laboratory analyses. The results of the QA analyses for each laboratory are reported in the respective sections below, with details provided in Appendix D.

3.8.1 In Situ Bioremediation Field Laboratory

Data generated by the ISB Field Laboratory are considered screening level data and are used as general indicators of changing geochemical conditions. The ISB Groundwater Monitoring Plan (INEEL 2003b) requires analysis of field duplicates, field blanks, standards, and standard additions (matrix spikes). Acceptable precision and accuracy targets are included in Technical Procedure (TPR) -166, “In Situ Bioremediation Field Analysis Procedure.” Although QA samples are required to be collected and analyzed at a specified frequency, the associated targets for accuracy or precision are established as an internal quality check. Definitive data are not required for the ISB Field Laboratory tests.

Geochemical parameters and nutrients were analyzed immediately after sample collection using Hach® field test kits. The results of these evaluations indicate that the field tests generally provide accurate and precise measurements, with the exception of COD, for which the accuracy required corrective action. COD standard recovery was within range for only 5 of 13 tests. Standards outside the range were all biased high and within a relative percent difference (RPD) of <5%, showing that the out-of-range standards were precise but not accurate. The out-of-range COD standards were all analyzed using the same standard lot number; therefore, new COD standard solution has been ordered. Sulfate standard recovery was within range for 46 of 49 tests. Iron standard recoveries were within range for 34 of 40 tests. All phosphate standard recoveries fell within range, and ammonia standard recoveries were within range for three of four tests. Standard addition tests (matrix spikes) for sulfate, phosphate, and ammonia also fell within range. Alkalinity standard addition recoveries were within range for 31 of 33 tests.

Field duplicate results proved the precision of the field test kit analyses. The RPD for COD was within range for 26 of 32 duplicate tests. The iron RPD was within range for 37 of 38 duplicate tests. The sulfate RPD was within range for 18 of 20 duplicate tests. All alkalinity RPDs fell within range, while the ammonia RPD was within range for three of five duplicate tests, and the phosphate RPD was within range for four of five duplicate tests. There was no blank contamination found for ISB Field Laboratory analytes during this reporting period.

3.8.2 INL Research Center Laboratory

Analyses for VOCs, dissolved gas, and electron donor constituents are performed at the IRC. These data are considered screening level data where rapid turn-around times and economical analyses are an important consideration. The ISB Groundwater Monitoring Plan (INEEL 2003b) requires field duplicates and blanks and also requires the laboratory to perform initial and continuing calibration checks as well as analysis for matrix spike and matrix spike duplicates (MS/MSDs).

During this reporting period, split samples from each well were sent to the off-Site laboratory on a semi-annual basis to address the Groundwater Monitoring Plan requirement for independent verification of the IRC VOC results. As had been reported in previous years, the results of split samples analyzed off-Site by Method 8260B (EPA 1996) were significantly different than the results obtained using the solid-phase microextraction (SPME) method at the IRC. However, with the exception of cis-DCE, the majority of the VOC split samples had relative differences less than 50%. The results of the SPME analysis were both above and below the 8260B results; there was no apparent bias. Details of the split sample analysis are presented in Appendix D.

Because the differences between split sample results could be attributed to a number of factors, a more definitive measure of accuracy of the IRC laboratory methods is provided by using performance evaluation (PE) samples. On a monthly basis, commercially supplied, certified PE standards were included with the groundwater samples submitted to the IRC laboratory. Both high (>100 ppb) and low (<100 ppb) concentration standards were used to evaluate method accuracy in concentration ranges. The following results were out of range for the IRC PE samples: six out of 20 high-range and two out of 24 low-range PCE; four out of 20 high-range and one out of 24 low-range TCE; two out of 20 high-range and six out of 24 low-range cis-DCE; two out of 20 high-range and one out of 24 low-range trans-DCE; and eight out of 20 high-range and 10 out of 24 low-range VC. The results of the PE sampling program indicate that the SPME method used at the IRC is accurate for the contaminant of concern, TCE. Accuracy decreases for the TCE degradation daughter products; however, these data are used for trending purposes and concentrations are not detected within some of the ranges (e.g. high range VC).

Precision of the VOC and dissolved gas data also was evaluated by comparing results of duplicate samples. The RPD for TCE ranged from 1 to 5%, which met the TCE precision requirement of 14%. For all other VOC and dissolved gas, 84% of the duplicate samples had an RPD of <25%. For the blanks collected during this reporting period, no significant detections were reported with the exception of methane in the field blanks and trip blanks. A deionized (DI) water system that uses TAN potable water to generate DI water was installed in May 2004; shortly thereafter, this water was used for trip and field blanks. The presence of methane in the blanks coincides with the use of TAN potable water to generate DI water. It is likely that the methane in the blanks originates from the potable water at TAN.

3.8.3 Off-Site Laboratories

Semi-annual split samples are sent to off-Site laboratories for definitive confirmation of VOC concentrations. Three of the five off-Site TCE duplicate samples met the target RPD of 14%. For the remaining VOC analytes, the RPD ranged from 0 to 100%. Standard and matrix spike recoveries were evaluated as part of the Level A data validation. MS/MSD sample recoveries fell within range for all TCE analyses. In addition to the laboratory prepared spikes, two commercially prepared PE samples were submitted to the off-Site laboratory for VOC analysis in November 2003 and May 2004. The November sample was a low value (<100 μg/L) VOC sample and the May sample was a high value (>100 μg/L) VOC sample. Both PE samples were within range for all analytes. The QA results for radionuclide samples sent off-Site are detailed in Appendix D. Tritium and Sr-90 duplicate sample results ranged from 0 to 65%, with one outlying tritium result.

4. DISCUSSION

This section discusses the results of the routine sodium lactate injections conducted from November 2003 to February 2004. The results for the AED optimization conducted from March to September 2004 are presented in Section 3 of this report. Results from the two baseline sodium lactate injections (conducted in March 2004 and May 2004) will be discussed below; however, the results from the first whey powder injection will not be discussed in this report. Results from the whey powder injections conducted as part of the AED optimization will be evaluated following the completion of the AED optimization in June 2005. Section 4.1 discusses the effectiveness of ISB operations, including electron donor distribution, degradation, and utilization in relation to ARD efficiency observed following the sodium lactate injections. Section 4.2 discusses the enhanced dissolution of source material and ARD. Effects of injections on radionuclide migration are presented in Sections 4.3.

4.1 Effectiveness of Sodium Lactate Injections

This section discusses the overall effectiveness of ISB operations using sodium lactate observed during the reporting period in comparison to data collected during past ISB operations. During this reporting period, two sodium lactate injections in TSF-05 and two sodium lactate injections into TAN-1859 were monitored at approximately 1- and 5-week intervals following the injections, and two sodium lactate injections in TSF-05 as part of the AED optimization were monitored at an increased frequency, which included sampling events approximately on Days 2, 4, 8–10, 22 or 23, and 36–38 following the injection. The effectiveness of the alternating injection strategy between TSF-05 and TAN-1859 is also evaluated in this section.

4.1.1 Sodium Lactate Distribution and Degradation

One of the main objectives of ISB operations at TAN is to create a biologically active area that encompasses the entire residual source area. In this biologically active area, contaminants are efficiently degraded to innocuous end products, and the flux of contaminants to downgradient locations is effectively stopped. Injections into TSF-05 alone have not yet achieved complete encapsulation of the residual source area, as indicated by continued TCE flux to TAN-37. Therefore, this reporting period began with alternating sodium lactate injections between TSF-05 and TAN-1859. From November 2003 through February 2004, 1X 6% sodium lactate injections into TSF-05 were conducted on November 3, 2003 and January 6, 2004; a 1X 6% sodium lactate injection into TAN-1859 was conducted on December 1, 2003; and a 2X 3% sodium lactate injection was conducted on February 9, 2004. This injection strategy was implemented based on results of the 4X injections performed during 2002 and 2003, which showed increased and persisting concentrations of cis-DCE at Wells TAN-25 and TAN-31. This suggested that the 4X injection strategy was having a negative impact on dechlorination efficiency within the biologically active zone near the injection point (Armstrong et al. 2004). Therefore, smaller volume (1X or 2X) injections were alternated between the two injection locations using nominal concentrations of sodium lactate at 3 or 6%. The distribution and degradation of sodium lactate following each of these injections is presented below.

The electron donor distribution was evaluated to determine the radial area of influence achieved through each injection location. Based on the data presented in Section 3 of this report, the two 1X 6% injections into TSF-05 in November 2003 and January 2004, as well as two 1X 6% injections in TSF-05 in March 2004 and May 2004, distributed electron donor across a radial distance of approximately 100 ft from the injection point. Following each injection, significant concentrations of electron donor reached TAN-1859 (90 ft downgradient of the injection well TSF-05). These injections continued to maintain reducing conditions appropriate for ARD of TCE to ethene in the biologically active wells but failed to

significantly impact TCE concentrations at TAN-37, suggesting that the entire residual source had not been influenced. This was consistent with findings from previous reporting periods, which showed that injection into TSF-05 alone were not able to effectively distribute donor to the downgradient edge of the residual source (Armstrong et al. 2004; INEEL 2002a; INEEL 2003a).

The radial distribution of sodium lactate as a result of the December 1, 2003 1X 6% injection into TAN-1859 could not be effectively determined. TAN-1859 was the only location where electron donor and geochemical changes were observed following the injection. Even at TAN-1859, high concentrations of electron donor were not observed until a lower depth was sampled. This suggests that significant vertical transport of the electron donor solution had occurred within the well. Therefore, a 2X 3% sodium lactate injection was conducted on February 9, 2004. The COD concentrations at TAN-1859 following this injection suggest that electron donor was more effectively delivered to the upper extent of the aquifer. Again, however, the lateral extent of electron donor distribution following the 2X 3% injection into TAN-1859 is unknown because neither electron donor, nor geochemical changes were observed at any other sampling location. There may have been some influence to VOC concentrations at TAN-37 as a result of injections into TAN-1859, although the results are tentative (see discussion below in Section 4.2). The injections into TAN-1859 appear to be minimally effective at best, owing to the apparent vertical transport within the injection well, and to distribution of the electron donor to areas not within the monitoring zone of the ISB well network (or presumably within the contaminant zone). In order for injections into TAN-1859 to be effective at cutting off flux to TAN-37, optimization of the injection strategy will be necessary. One option would be to install a packer into TAN-1859 to minimize the transport of the injection solution to the lower extent of the aquifer, and to distribute the majority of the electron donor to the upper extent of the aquifer where contaminants are present.

Injection of electron donor into the groundwater at TAN results in the degradation of the primary substrate injected (i.e. lactate) into secondary fermentation products, including VFAs and hydrogen, that can be further degraded by various members of the microbial community. It is important to understand the particular degradation reactions that occur in order to determine the distribution, fate, and longevity of the electron donor. Ultimately, the degradation of the primary substrate impacts microbes undergoing halorespiration of TCE to ethene because halorespiring bacteria identified at TAN actually use the fermentative daughter products hydrogen and acetate (He et al. 2003, Maymo-Gatell et al. 1997). It is possible that the preference of one pathway over another will result in differences in degradation of contaminants. The propionate to acetate ratio has historically been used to determine in which of two possible pathways lactate is fermented (see Section 3.1.1). One pathway produces propionate to acetate in a 2:1 ratio, while the other pathway produces acetate-only. Therefore, higher propionate to acetate ratios (range 0–2) indicate that lactate is being fermented in whole or part via the propionate pathway. During the ISB field evaluation in 1998–1999, the propionate to acetate ratio was 2, which suggested that all of the lactate was being fermented by the propionate pathway. Over time, the propionate to acetate pathway has declined, and the values reported following the November 2003 (0.56) and January 2004 (0.51) injections into TSF-05 suggest that the acetate pathway is currently the predominant pathway. Similar results were also observed following the AED March and May 2004 injections. The propionate to acetate ratio in TAN-1859, however, following the December 2003 and February 2004 injections (1.41 and 1.20), suggests that the propionate pathway is more predominant at this location. This suggests that the microbial community at this location is more similar to the original community near TSF-05 that was active during the field evaluation.

Since results following only one of the AED optimization whey injections are presented in this report, a detailed description of the degradation of lactose into daughter products on a molar basis will be presented and discussed once the AED optimization is complete. The fermentation pathways are still being researched, and a conceptual model describing whey degradation in TAN groundwater is being developed. In addition, the transformation of lactose may change over time as the microbial community

transitions from one dominated by members using lactate (i.e. sodium lactate) to members using whey powder (i.e. lactose).

4.1.2 Sodium Lactate Utilization

Optimization of the ISB process includes analysis of electron donor utilization, which was assessed using electron donor degradation rate constants. The utilization of the electron donor directly influences the frequency of electron donor injections required to maintain conditions conducive to ARD in TAN groundwater. The goal of this process is to minimize the frequency of injections while maintaining a sufficient amount of electron donor to drive a relatively high rate of dechlorination. Detailed analysis of the first order degradation rate constants for lactate and COD was presented in Section 3.1.3.1 for the samples collected from biologically active wells.

Lactate utilization rate constants calculated at TAN-25 following the four 1X 6% sodium lactate injections, including two during the AED optimization baseline, were similar to historical sodium lactate utilization rate constants calculated at TAN-25 following the 1X 6% sodium lactate injections (Figure 4-1). Therefore, the utilization rates for lactate were very reproducible, even when including the additional data points collected during the AED optimization. For Well TSF-05, the 1X 6% concentration injections resulted in lactate and COD utilization rates that were similar to rates calculated from previous reporting periods. For example, the calculated lactate rate constants generated from 1X 6% injections in July through September 2003, ranged from 0.27 to 0.51 (Armstrong et al. 2004), which were comparable to those generated from November 2003 and January 2004 lactate injections (0.28–0.35). Therefore, lactate utilization across the biologically active area appears to be fairly stable for this injection strategy; results indicate lactate was being depleted between approximately 18 and 36 days (using 0.27 and 0.51), assuming 15,000 mg/L lactate as an initial concentration. In addition, the COD degradation rate constants for the biologically active wells (0.12 to 0.18) were similar to those reported following previous 1X 6% injections, which ranged from 0.13 to 0.17 (Armstrong et al. 2004). Well TAN-25 is presented as an example (Figure 4-2). This would result in a depletion of total COD between 53 and 80 days after injection (using 0.12 and 0.18) assuming 15,000 mg/L as COD for the initial concentration. These data suggest that the injection frequency needed to maintain electron donor within the biologically active area is approximately 7 to 11 weeks.

4.2 Anaerobic Reductive Dechlorination

In the 2003 ISB Annual Report (Armstrong et al. 2004), accumulation of cis-DCE suggested that the ARD efficiency within the biologically active area had decreased because of the high-volume 4X 3% sodium lactate injections. As a result of resuming 1X 6% sodium lactate injections, ARD efficiency (as measured by ethene accumulation) increased at these locations as well as at TSF-05. Following each injection event, increased concentrations of total chloroethenes were observed, followed by complete conversion to ethene at all of the biologically active wells, as a result of degradation by indigenous microbial populations. Efficient ARD also was observed following each injection into TAN-1859, as cis-DCE and VC were converted into ethene following each injection cycle. TCE at TAN-1859 has been nondetect since December 2003. Total molar concentrations of chlorinated ethenes and ethene, which includes: TCE, cis-DCE, VC, and ethene, also followed the same trends previously reported (Armstrong et al. 2004).

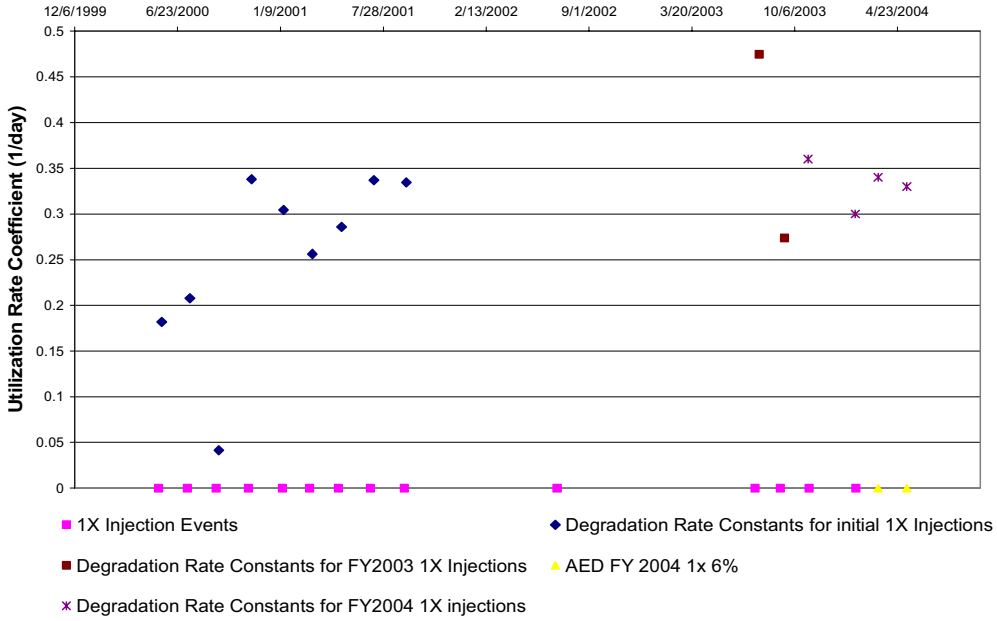

Figure 4-1. Lactate utilization rate constants at Well TAN-25 following the 1X 6% sodium lactate injections.

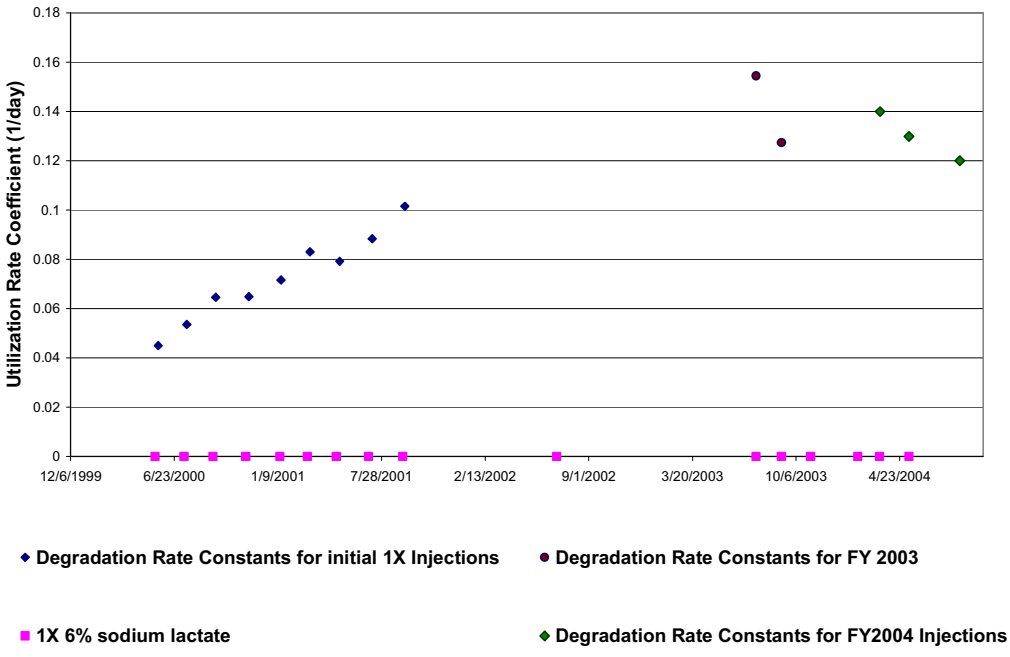

Figure 4-2. Chemical oxygen demand utilization rate constants at Well TAN-25 following 1X 6% sodium lactate injections.

Sodium lactate injections into TAN-1859 during this reporting period may have resulted in temporary declines in total chloroethene concentrations at Well TAN-37. For example, at TAN-37A and TAN-37B, TCE concentrations declined below 100 µg/L following the injection into TAN-1859, with TCE concentration lows at the May 17, 2004 (67 and 56 µg/L) sampling event (approximately 3 months after the last injection). These concentration declines also occurred 1 month following an injection into TSF-05. As a result, the concentration declines may have resulted from that injection, the injection into TAN-1859, or a combination of the two. TCE concentrations, however, subsequently rebounded. The chloroethene reduction also did not coincide with observable changes in the geochemistry at these locations. Therefore, the correlation between the injection into TAN-1859 and the reduced chloroethene concentrations is speculative until further data can be collected. None of the deep, downgradient, or outside wells showed evidence of active ARD.

4.3 Enhanced Dissolution of Residual Source Material

Enhanced mass transfer of TCE from the residual source material into the aqueous phase is the rate-limiting factor affecting the remedial timeframe for ISB at TAN. Optimization of ISB operations, therefore, includes an evaluation of the mechanisms that affect this dissolution rate, including enhanced dissolution of TCE from the residual source following high-concentration electron donor injections, as well as maximizing the concentration gradient between non-aqueous contaminants and the aqueous phase via efficient ARD.

Historically, high concentration sodium lactate injections have resulted in spikes in total chloroethene and ethene concentrations at well locations impacted by the electron donor injections. After each injection, the subsequent stoichiometric conversion of TCE to cis-DCE and ethene demonstrates that the newly liberated TCE is efficiently degraded to innocuous end products. Historical trends in total VOCs observed following 1X 6% sodium lactate injections were assessed by calculating the areas under the molar VOC curves using data collected at the 1- and 5-week sampling events throughout the project history (Figures 4-3 through 4-5). By calculating the areas under the VOC curves (see Figures 3-8 through 3-11), the subsequent units are in molar concentration multiplied by the number of days (M*d), which is the y axis of the charts. These calculations only consider the total area over an injection cycle and therefore include both mass liberated as a direct result of enhanced dissolution via electron donor injection and dissolution due to ARD activity.

The area under the VOC curve can be used to assess a relative impact of the individual injection events at different monitoring locations within the residual source area. The larger the area (M*d) under the VOC plots, the greater the contaminant mass that is degraded between injection events. Because the analysis is relative, only the historical 1X 6% injection events were evaluated. Overall, a declining trend in total area, or residual source impact, can be observed when assessing the relative impact of 1X 6% injections that occurred in 2000 compared with 1X 6% injections that occurred in 2004 (Figures 4-3 through 4-5). During the AED optimization baseline sodium lactate injections, additional data points allowed for a better assessment of the VOC area under the curve. The VOC area under the curve calculated using the additional data were very similar to those calculated using only the 1- and 5-week data points (see Figures 4-3 through 4-5). This suggests that the AED data can be compared to the historical data, even though less data were collected (i.e. fewer sampling events between injections).

These data suggest that the efficiency of the 1X 6% injection strategy has declined overall during ISB operations. For instance, at TSF-05B and TAN-25, a nearly linear decline in the area under the VOC curves was observed during the 1X 6% injections conducted May 23, 2000 through July 23, 2001. In contrast, the VOC area has remained fairly consistent for 1X 6% injections that occurred between July 29, 2003 and May 18, 2004, but at significantly lower levels for TSF-05A and B. This suggests that at the beginning of ISB operations, the most contactable source material was liberated and destroyed first,

resulting in a rapid decline in the total mass liberated into the aqueous phase following each successive injection cycle. Once the most accessible source material was gone, equilibrium was reached for the flux of contaminants from the existing source material following each injection. A major goal of the AED optimization is to determine whether a step-change could be made in this equilibrium mass removal rate to shorten the overall remedial timeframe.

4.4 Effect of Injections on Radionuclide Migration

Monitoring radionuclide concentration trends in the groundwater at TAN provides the ability to track any potential source mobilization. Past reports have shown evidence of radionuclides being mobilized resulting from amendment injections in the vicinity of TSF-05, but they were rapidly attenuated before reaching locations downgradient of the biologically active area. Concentrations of strontium-90 had slight fluctuations, but overall have remained stable during this reporting period. Tritium concentrations also remained relatively stable throughout the reporting period. Overall, radionuclide concentrations have remained at similar or lower concentrations compared to radionuclide concentrations presented in past ISB annual reports.

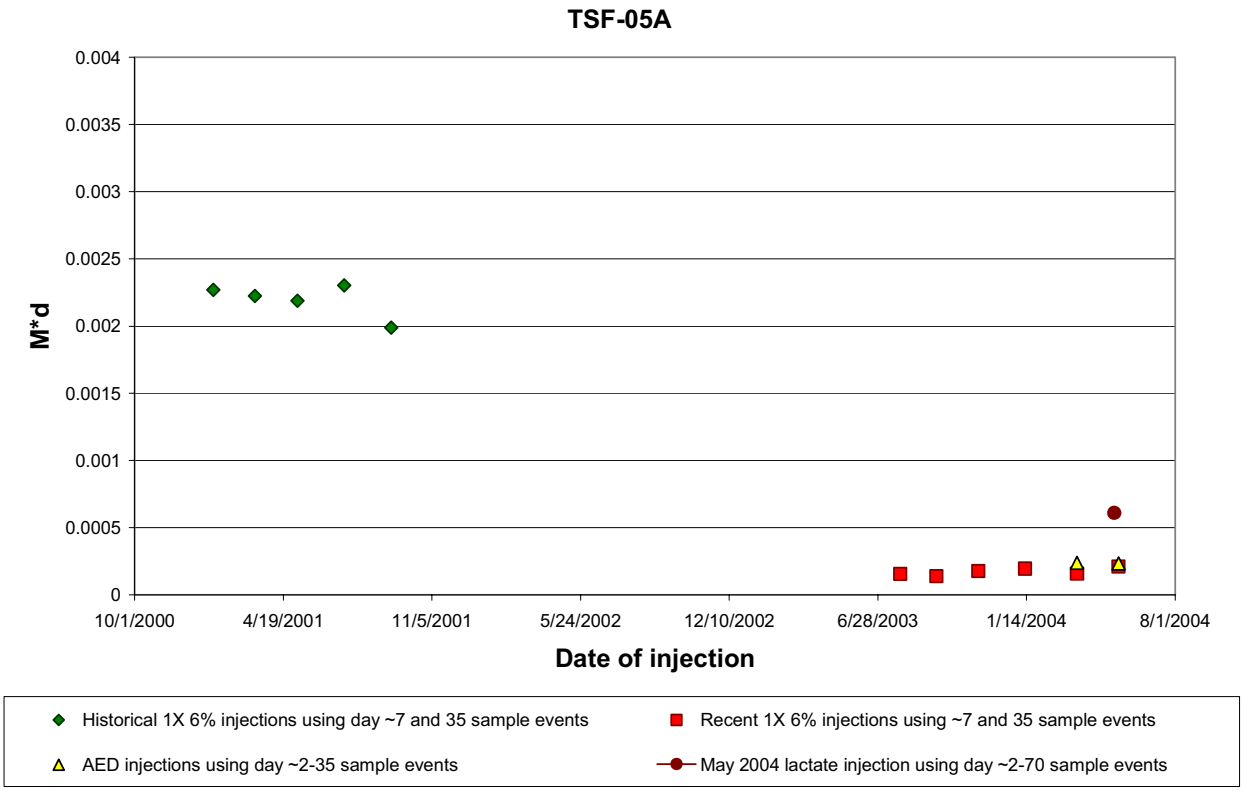

Figure 4-3. Volatile organic compound areas calculated between injection events at TSF-05A using the 1- and 5-week sampling events and the high-frequency alternate electron donor sampling events for the 1X 6% sodium lactate injection strategy.

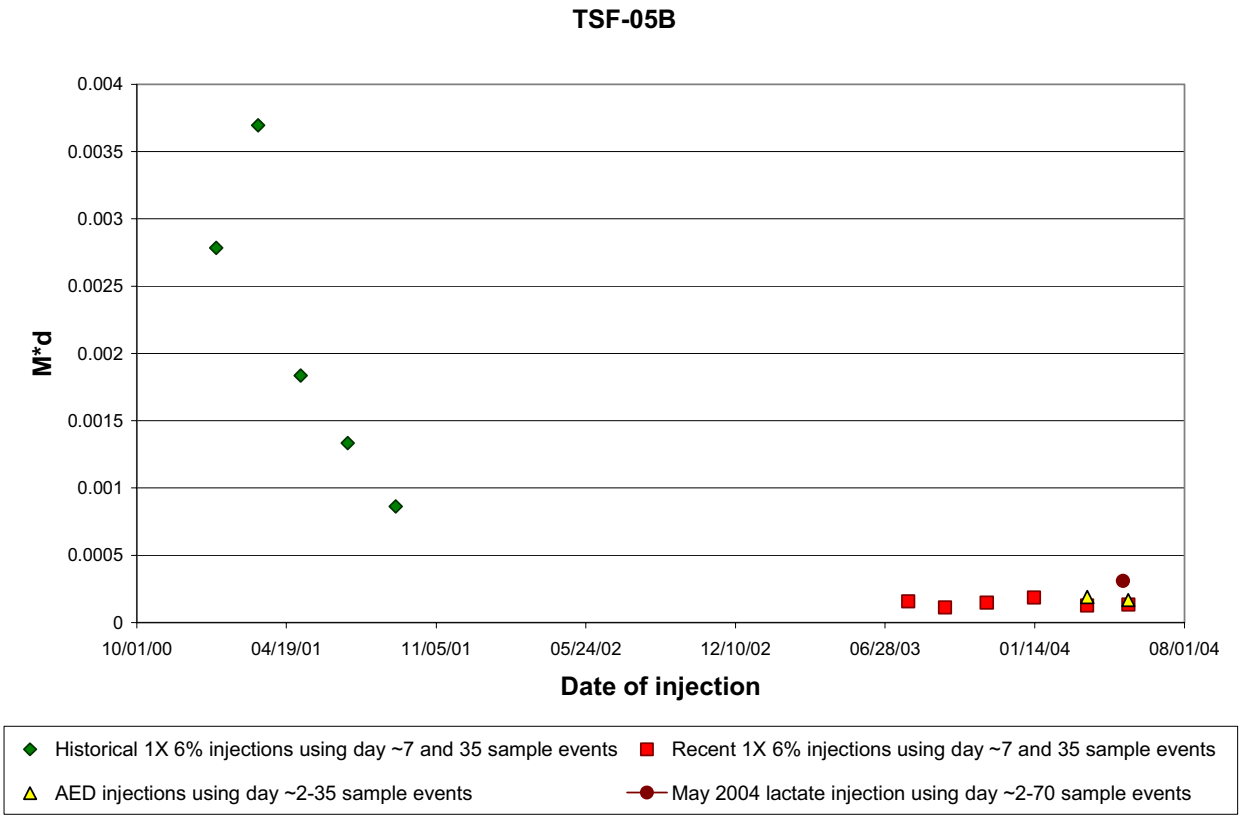

Figure 4-4. Volatile organic compound areas calculated between injection events at TSF-05B using the 1- and 5-week sampling events, and the high frequency alternate electron donor sampling events for the 1X 6% sodium lactate injection strategy.

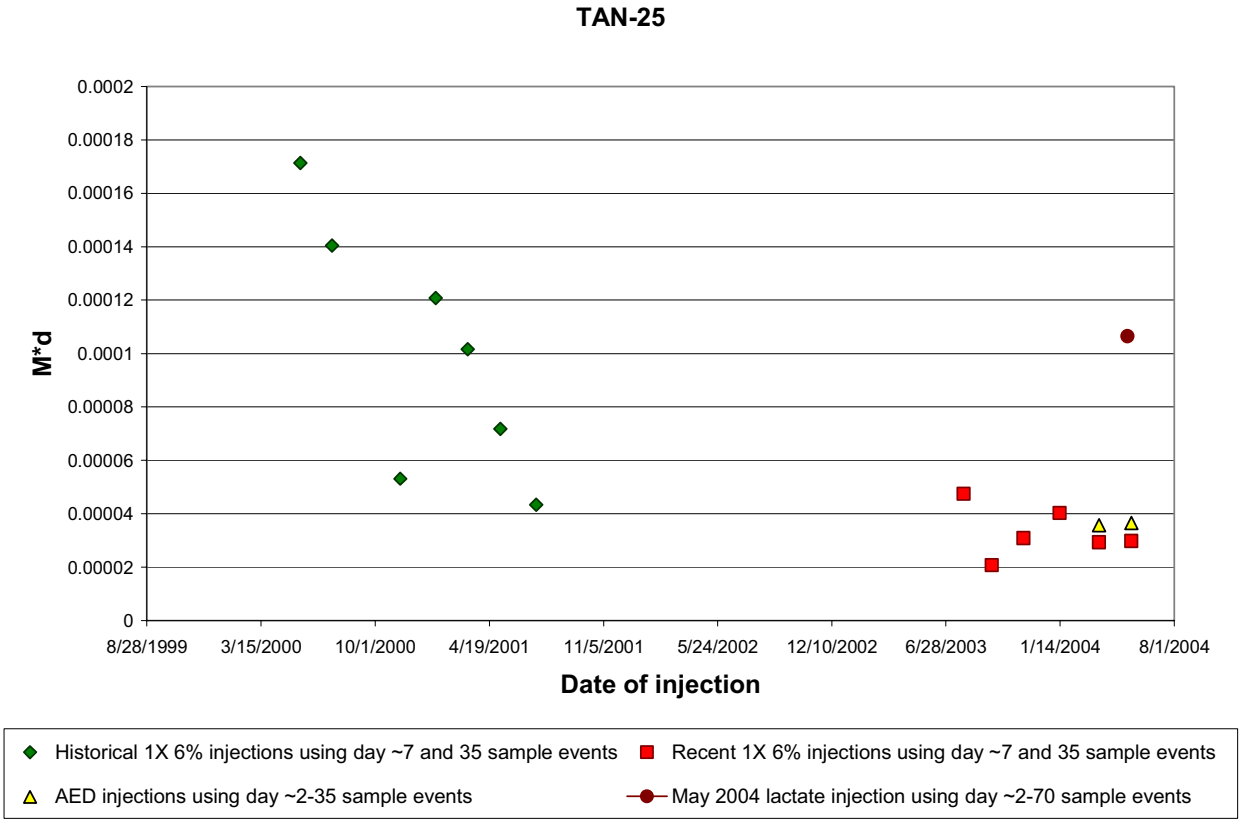

Figure 4-5. Volatile organic compound areas calculated between injection events at TAN-25 using the 1- and 5-week sampling events, and the high frequency alternate electron donor sampling events for the 1X 6% sodium lactate injection strategy.

5. CONCLUSIONS

The ultimate goal of Operable Unit 1-07B remedial activities is to achieve the remedial action objectives specified in the Record of Decision Amendment (DOE-ID 2001). Activities conducted during this reporting timeframe demonstrate progress toward the remedial action objectives. The timeframe of this ISB annual report coincides with the first year of activities conducted as part of the Initial Operations Phase.

In general, the ISB remedy continues to operate effectively, stimulating ARD throughout most of the source area. Ethene was present in significant concentrations in all biologically active wells, indicating active ARD. The two ISB strategies implemented during this reporting period included (1) alternating monthly sodium lactate injections in TSF-05 and TAN-1859, and (2) initiation of an AED optimization to evaluate the effectiveness of whey powder as compared to sodium lactate. The alternating injections of sodium lactate between TSF-05 and TAN-1859 demonstrated that injections into TSF-05 distributed electron donor across a radial distance of approximately 100 ft from the injection point and continued to maintain reducing conditions appropriate for ARD of TCE to ethene. Distribution of electron donor following injections into TAN-1859, however, could not be effectively determined because of significant vertical transport of the sodium lactate injection solution within the well. As a result, the only monitoring location where electron donor was detected was TAN-1859. The increased sampling frequency conducted as part of the baseline phase of the AED Optimization provided additional information to assess the impacts of two sodium lactate injections into TSF-05. Ultimately, these data will be used to compare to similar data collected following whey powder injections. The results of the AED optimization activities conducted during this reporting period will be discussed following completion of the AED optimization.

The goal of the Initial Operations Phase is to eliminate flux of contaminants from the source area to downgradient locations, specifically TAN-28 and TAN-30A. Continued monitoring of the ISB wells will provide data to determine how effectively certain electron donor injection strategies encompass the entire source area, sustain efficient ARD conditions, and arrest flux of contaminants from the residual source. Recommendations from activities conducted during this reporting period that will improve the capability to cut off downgradient flux are stated in Section 6.

6. RECOMMENDATIONS

The following recommendations are made based on the results and discussions presented in this report:

- Continue the Initial Operations Phase of ISB.
- Complete the AED optimization.
- Following completion of the AED optimization, an electron donor will be chosen for use during future injections. In order to target specific source areas and control vertical distribution of electron donor during injections, it is recommended that a packer be installed in TSF-05 in an attempt to distribute electron donor into the upper portion of the aquifer.
- Continue operations of the in situ water quality instrument network for the remainder of the AED optimization. Evaluate reducing the network for future injections.
- Continue the monthly PE sample program for VOC analyses conducted at the IRC; include PE samples with each shipment of VOC samples sent to off-Site laboratories to provide continued comparison between the SPME and U.S. Environmental Protection Agency (EPA) 8260B methods.
- Following completion of the AED optimization, consider modifications to the ISB monitoring strategy. Modifications could include reduction in sampling frequencies and analytes for some ISB wells and changes to the ISB quality assurance requirements.

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